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JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Refractometric Observations. By J. F. EYKMAN (*Ber.*, **25**, 3069—3079).—The author has determined the refraction and dispersion equivalents of a considerable number of isomerides with a view of drawing conclusions as to their constitution from the values of their molecular constants. The measurements were made for the lines $H\beta$ and $H\alpha$. His results for the molecular refraction and dispersion calculated by means of Gladstone's and of Lorenz's formulæ are given in the following table:—

	Molecular refraction for A.		Molecular dispersion from H_β and H_α.	
	Gladstone.	Lorenz.	Gladstone.	Lorenz.
Piperidine, $C_5H_{11}N$	43·42	26·01	0·87	0·45
$C_6H_{13}N$.				
1. Methylpiperidine	51·50	30·96	1·10	0·57
2. Methyl-α-methylpyrrolidine	51·24	30·89	1·09	0·56
3. $\alpha\alpha_1$-(2, 5) Dimethylpyrrolidine (Tafel)	50·97	30·70	1·01	0·53
4. Butallylmethylcarbinamine	52·99	31·92	1·20	0·63

	Molecular refraction for A.		Molecular dispersion from H_β and H_α.	
	Gladstone.	Lorenz.	Gladstone.	Lorenz.
$C_7H_{15}N$.				
1. Methyl-α-pipecoline—				
(*a*.) From pentallylcarbindimethylamine	58·74	35·28	1·24	0·65
(*b*.) From Ladenburg's pipecoline.....	58·62	35·18	1·24	0·64
2. Methyl-$\alpha\alpha_1$-dimethylpyrrolidine	58·63	35·30	1·21	0·63
3. Dimethylpiperidine	60·71	36·68	1·41	0·74
$C_8H_{17}N$.				
1. Pentallylcarbindimethylamine	68·40	41·26	1·58	0·82
2. Butallylmethylcarbindimethylamine	68·01	40·99	1·51	0·80
$C_9H_{15}N$.				
1. α-Methyltropidine	73·23	43·29	2·27	1·13
2. β-Methyltropidine	75·79	44·39	2·54	1·23
C_6H_{10}.				
(*a*.) Diallyl (b. p. 60—61°).	46·33	28·08	1·26	0·67
(*b*.) ,, (b. p. 80—83°).	47·85	28·72	1·80	0·92
Tropilidene, C_7H_8	51·50	30·32	2·06	1·00
Tropilen, $C_7H_{10}O$.....	53·05	31·45	1·46	0·72
Tropidine, $C_8H_{13}N$	61·73	36·59	1·41	0·71
Tropine, $C_8H_{13}NO$.....	64·62	38·29	1·18	0·60
Ecgonine, $C_9H_{15}NO_3,H_2O$	79·90	46·44	1·56	0·75
Pseudotropine (= Oscine)—				
(*a*.) Calc. for $C_8H_{15}NO$ (Ladenburg)	58·49	34·91	1·05	0·46
(*b*.) Calc. for $C_8H_{13}NO_2$ (Hesse, Schmidt)....	64·30	38·38	1·16	0·50
Acetonylacetone, $C_6H_{10}O_2$ ...	48·91	29·51	0·97	0·51

These results the author discusses in reference to the probable constitution of the substances, and finds that they agree in general with the views expressed by Merling (Abstr., 1891, 1506), from whom most of the specimens examined were obtained. J. W.

Physical Character of the Lines in the Spark Spectra of the Elements. By W. N. Hartley (*Proc. Roy. Soc.*, **49**, 448—451).—Perrot has shown that the spark discharge is composed of two parts: the fiery track or central portion is a statical discharge, whilst the aureole or flame is dynamic and capable of electrolytic action.

From observations of the sparks and photographs of the spectra, the author considers that the principal lines lying between point and point of the electrodes are spectra of the fiery path of the spark; the extension of the principal lines above and below the points of the electrodes seem to be spectra of the aureole. Elements which are difficultly volatile, and those which are bad conductors, do not exhibit

spectra with extended lines, and, conversely, metals which are the best conductors, and the most volatile, give spectra with their principal lines largely extended. The metals magnesium, zinc, cadmium, aluminium, indium, copper, silver, and mercury are the best conductors, and consequently show considerable extension of their principal lines. With these metals, the continuous specturm is very weak, and in the cases of thallium and mercury, the air spectra are suppressed by the dense vapours in the track of the spark. The extension of the lines is even observed with concentrated solutions of the metals.

The nimbus seems not to be wholly dependent on the volatility or readiness with which the metal is oxidised, although volatility certainly increases the nimbus. Amongst the photographed spectra, that of magnesium shows the largest nimbus, owing probably to the great actinic power of the rays emitted, and also to the large quantity of the metal in the track of the spark. After magnesium, cadmium and mercury exhibit the largest nimbus; those of platinum, gold, copper, and silver are small. There is a considerable nimbus about some of the lines of arsenic, antimony, bismuth, tin, and lead, and but very little about those of thallium and iridium. The nimbus is evidently an expression of the quantity of matter in the spark, and of the chemical activity of the rays emitted by the ignited vapour.

The continuous spectrum, which forms the background to the lines of certain spectra, must be due to the ignition of some solid substance or oxide. The spectra of gold, silver, platinum, mercury, iridium, zinc, and cadmium, metals which either are not oxidisable or form volatile oxides, do not have this background; the less metallic elements, tellurium, arsenic, antimony, and bismuth, however, show it very strongly. No sufficient explanation of this has yet been given.

The breadth of the principal lines in the photographed spectra is dependent on the actinic power, volatility, vapour density, and electrical conductivity of the metal. In accordance with this, the lines of cadmium are broader than those of zinc, which are in turn broader than those of magnesium. W. J. P.

The Planté Lead | Sulphuric Acid | Lead Peroxide Cell from a Chemical Standpoint. Part I. By G. H. Robertson (*Proc. Roy. Soc.*, **50**, 105—108).—The author was unable, either directly or indirectly, to obtain any evidence of the existence of an oxysulphate of lead corresponding with red lead; there is, therefore, no ground for supposing that the ordinary lead sulphate is not the only one concerned in the reactions occurring in the Planté cell. If the sudden lowering of the E.M.F. were caused by a change in the nature of the chemical compounds formed on the plates, it would be difficult to account for the very rapid recovery of the E.M.F. exhibited by an apparently discharged cell.

It would seem that the different behaviour of secondary cells containing sodium sulphate (1 per cent.) and cells containing none is due to the catalytic action of this salt on the hydrogen peroxide always found in the electrolysed acid of the strength used in such batteries, which is probably formed from persulphuric acid. Cells containing sodium sulphate show much less sulphating than do

ordinary cells, and the addition of this salt (1 per cent.) to the freshly electrolysed acid is always attended by a diminution in the amount of hydrogen peroxide. The acid taken from secondary cells reduces lead dioxide, and if hydrogen peroxide be added to the acid in the cells, an annulment or reversal of the E.M.F. occurs, whilst the introduction of hydrogen peroxide into the body of the dioxide paste produces an increase of E.M.F. in the case of a platinum | lead dioxide couple. The pink colour assumed by the acid in the Planté cell is due to the formation of permanganic acid from impurities in the lead.

W. J. P.

The Planté Lead | Sulphuric Acid | Lead Peroxide Cell from a Chemical Standpoint. Part II. Discussion of the Chemical Changes occurring in the Cell. By H. E. ARMSTRONG and G. H. ROBERTSON (*Proc. Roy. Soc.*, **50**, 108).—The authors arrive at the following conclusions:—(1.) That the cooling observed in the Planté cell can only be explained as resulting from the dissociation of the dilute sulphuric acid. (2.) That the observed loss in efficiency cannot be due to temperature changes, as these arise through actions occurring out of circuit. (3.) That if sulphating occurs at both plates in circuit and under the influence of sulphuric acid, the calculated E.M.F. is considerably higher than the observed value, whilst, if sulphating occur only at the lead plate, the calculated E.M.F. is far too low. This comparison, therefore, leads to no conclusion as to the exact nature of the changes which take place in the cell. (4.) That a counter E.M.F. of about 0·5 volt would account for the observed departure from the highest calculated value. Such a counter E.M.F. may exist, peroxides being always present in the electrolyte. (5.) That the observed loss of efficiency is due to the formation of peroxides in the electrolyte, and to the excessive sulphating occurring chiefly at the dioxide plate in the local circuit existing between the support and the paste.

W. J. P.

Electrolysis of Silver Nitrate in a Vacuum. By A. SCHUSTER and A. W. CROSSLEY (*Proc. Roy. Soc.*, **50**, 344—358).—The deposit of metallic silver obtained on electrolysis of silver nitrate solution in air, increases slightly in weight as the current density at the platinum cathode decreases. The authors find that this difference is persistent when the deposition occurs in a vacuum. The deposit is slightly increased in weight if electrolysis proceeds under diminished pressure; this is due to the withdrawal of oxygen, for if the solution be electrolysed in an atmosphere of this gas, a heavier deposit is obtained than in air.

The authors conclude that the true electrochemical equivalent of silver is probably not quite 0·1 per cent. greater than the value assigned to it by Rayleigh.

W. J. P.

Electrolytic Dissociation and Ionisation. By J. TRAUBE (*Ber.*, **25**, 2989—2993; compare Abstr., 1891, 255, 390, 638).—The author now practically adopts the hypothesis of electrolytic dissociation to explain the behaviour of aqueous salt solutions, contending, however, that the dissociation into ions need not be complete dis-

sociation, but only a slackening of the bonds which hold the ions together. This modified dissociation he calls, after Fitzgerald, ionisation. J. W.

Absorption of Radiant Heat by Alum. By C. C. HUTCHINS (*Amer. J. Sci.* [3], **43**, 526).—It is a generally accepted opinion that a solution of alum acts as a particularly efficient absorber of rays of great wave-length; but the author shows by direct experiment that a solution of alum is really no better absorber than water, and that, furthermore, it would hardly pay to use plates of transparent alum, even if they were to be had. H. C.

Specific Heat of Carbonic Anhydride. By N. S. KURNAKOFF (*J. Russ. Chem. Soc.*, **22**, 493—495).—From the apparent specific heat of carbonic anhydride at high temperatures (above 2000°) the author calculates the true specific heat by means of the formula $c = \frac{Ct - k(W + c_1 t)}{(1 - k)t}$, in which c is the true specific heat of carbonic anhydride, C the apparent specific heat, c_1 the mean specific heat of its products of dissociation (carbonic oxide and oxygen), W the heat of formation of carbonic anhydride from its dissociation products at 0°, k the coefficient of dissociation, and t the temperature. The following table of results is given by the author. In it, the values of c_1 are taken from Vielle's data, and the values of k are those given by Le Chatelier. W = 68,000 cal.

t.	C.	c_1.	k.	c.
2000°	19·1	9·0	0·035	18·3
2500	19·8	9·2	0·14	17·1
3000	20·6	9·4	0·3	15·7
3500	21·3	10·6	0·4	15·5
4000	22·1	11·5	0·45	17·0
4500	22·8	12·3	0·6 (?)	16·0

The true specific heat would thus seem to reach a minimum value at about 3500°. J. W.

Heat of Combustion of Chlorine Compounds. By BERTHELOT and MATIGNON (*Compt. rend.*, **115**, 347—350).—

	Heat of combustion. Const. vol.	Molecular heat of combustion.		Heat of formation.
		Const. vol.	Const. press.	
Chloracetic acid	—	+174·2 cal.	+173·9 cal.	+123·0 cal.
Trichloracetic acid	—	+106·3 „	+105·4 „	+132·1 „
Dichlorotrimethylene ...	3900 cal.	+432·8 „	+433·1 „	−2·6 „

The substitution of chlorine for hydrogen in acetic acid develops +25·3 Cal.; the substitution of 3 atoms of chlorine for 3 atoms of hydrogen in acetic acid develops +26·1 × 3 Cal. These numbers are somewhat lower than in the case of the substitution of chlorine for hydrogen in methane, the difference being probably due to the presence of oxygen.

The substitution of 2 atoms of chlorine for hydrogen in trimethylene develops $+34 - x$ Cal., x being the heat of formation of the hydrocarbon. C. H. B.

Glyoxylic or Dihydroxyacetic Acid. By BERTHELOT and MATIGNON (*Compt. rend.*, **115**, 350—353).—The experiments were made with a crystallised specimen of glyoxylic acid which had lost 0·213 mol. H_2O, and the final values were calculated on the assumption that recombination with this quantity of water would cause no thermal disturbance.

Heat of combustion of glyoxylic acid at const. vol. = +128·1 Cal., at const. press. 127·5 Cal., and consequently

$C_2 + H_4 + O_4 = C_2H_4O_4$ crystallised .. develops +199·1 Cal.
$C_2 + H_2 + O_3 + H_2O$ solid $= C_2H_2O_3,H_2O$ „ +128·7 „

The conversion of ethane into gaseous alcohol by direct oxidation would develop +34·6 Cal.; the oxidation of alcohol to aldehyde develops .+51·5 Cal., and of aldehyde into acetic acid +60·0 Cal. For the corresponding values in the cases of acetic, glycollic, and glyoxylic acids see following abstract.

As a rule, the substitution of HO for H in an acid, with production of an alcoholic function, develops from +35 to +45 Cal.

C. H. B.

Heat of Combustion of Glycollic Acid. By BERTHELOT (*Compt. rend.*, **115**, 393).—Stohmann points out that the heat of combustion of glycollic acid as determined by Louguinine (*Ann. Chim. Phys.* [6], **23**, 210—213) is +166·0 Cal., and not +186·0 Cal. It follows that the conversion of acetic acid into glycollic acid would develop +40·2 Cal., and the conversion of acetic acid into glyoxylic acid would develop +79·4 Cal. or +39·7 × 2. C. H. B.

Thermochemistry of Carbon Compounds of Mixed Function. By L. VIGNON (*Compt. rend.*, **115**, 354—356).—Experiments

	Heat of dissolution.	Heat developed by		
		1 mol. HCl.	2 mols. HCl.	3 mols. HCl.
$CH_2(C_6H_4\cdot NMe_2)_2$	+0·06 Cal.	+3·50	+2·35	+0·61
$CO(C_6H_4\cdot NMe_2)_2$	+0·26 „	+0·87	+0·00	+0·00
$CS(C_6H_4\cdot NMe_2)_2$	+0·22 „	+1·35	—	—

were made with tetramethyldiamidodiphenylmethane, tetramethyldiamidobenzophenone, and tetramethyldiamidothiobenzophenone.

The presence of the ketonic group CO destroys the basic function, but this effect is only partial in the case of the thioketonic group CS C. H. B.

Specific Gravity of Ice. By J. v. Zakrzevski (*Ann. Phys. Chem.* [2], **47**, 155—162).—It is pointed out by the author that the determinations of the specific gravity of ice at the freezing point are not sufficiently accurate for the purposes of exact heat measurement by means of Bunsen's ice calorimeter. By using a modification of this instrument, he has made fresh determinations of the specific gravity of ice at temperatures very near 0°. The calorimeter was filled with mercury and boiled-out water, the exact weight of which was ascertained. This water was frozen very slowly at a temperature just below the freezing point, the crystallisation being started at a given point by means of the external application of solid carbonic anhydride and ether. The mercury expelled was then weighed. A check determination was made by melting the ice and ascertaining the weight of mercury sucked up by the apparatus. The two weights usually differed by a few milligrams on a total of 15—30 grams. The results of the measurements are as follows:—

Temperature.	Specific gravity.
−0·705°	0·916710
−0·700°	0·916713
−0·699°	0·916708
−4·720°	0·916995

From these values, the specific gravity of ice at 0° is 0·916660, and the coefficient of expansion 0·000077. J. W.

Relation between the Specific Gravity of Acid or Saline Solutions and the Molecular Weight of the Dissolved Substances. By A. de Saporta (*Bull. Soc. Chim.* [3], **7**, 184—190).—An acid or saline solution made by dissolving 52·63 grams of substance in a litre of distilled water is termed a *typical solution*, and is usually of greater sp. gr. than water. The excess of the sp. gr. above unity is termed the *typical density A* (*alourdissement type*), and if a gram-molecule P of the substance is substituted for the constant amount, a quantity $AP/52·63$ is obtained which is termed the *theoretical molecular density*, and is held to be proportional to the *molecular excess* or difference between the molecular weight of the dissolved substance and that of water, $AP/52·63 = K(P - 18)$. From this it follows that $A/K = 52·63 - 947·34/P$, and the truth of the above supposition can be tested by comparing the values calculated from the right-hand side of the equation with those calculated from the left-hand side. The results are given for most of the commonly occurring inorganic acids and salts, and the agreement is fair, as a rule, when K is taken as unity, although more consistent results are obtained in some cases by giving it a higher value. Jn. W.

Specific Volume of Sulphur. By M. Toepler (*Ann. Phys. Chem.* [2], **47**, 169—174).—Monoclinic sulphur, plastic sulphur, obtained by rapid cooling from 140—170° to 20°, and liquid (syrupy) sulphur, obtained by very slow cooling through the same range of temperature, have been investigated by the author with respect to the volume they occupy at different temperatures.

His results are contained in the following table, the volume of liquid sulphur at 120° being taken as unity:—

	Monoclinic.	Liquid.	Plastic.
−20°	—	0·935	—
0	0·915	0·943	—
20	0·919	0·951	—
40	0·924	0·960	0·974
60	0·929	0·969	0·979
80	0·935	0·979	—
100	0·941	0·9889	—
120	—	1·0000	0·995
140	—	1·0117	1·001
160	—	—	1·007
180	—	—	1·014
200	—	—	1·021

J. W.

Relations between the Surface Tensions of Liquids and their Chemical Constitution. By C. E. Linebarger (*Amer. J. Sci.* [3], **44**, 83—92).—The author points out that up to the present little or nothing has been done towards establishing relations between the surface tensions of liquids and their chemical constitution. He proposes to investigate the subject, and the present paper is devoted mainly to a description of the method to be used in carrying out the experiments. This consists in determining the number of drops into which a certain volume of water divides in dropping down through liquids lighter than water, and in dropping up through liquids heavier than water, and the number of drops of a liquid dropping down, if heavier than water, and dropping up, if lighter, through that standard.

At the surface of two absolutely insoluble liquids, there would reign complete repulsion between the molecules; no molecule of one liquid would pass beyond a definite surface concentric with the surface of the liquids, and this surface would form an impenetrable barrier to molecules of each liquid. But in the case of liquids which dissolve one another a little, complete repulsion between the molecules prevails no longer, but, on the contrary, a slight attraction, so that now a molecule of one liquid may pass into the other. This would continue until the tension of solution of each liquid was reached. The question arises, whether the superficial tensions of liquids, saturated with each other, or pure, should be employed. In this preliminary investigation only the superficial tensions of liquids uncontaminated with one another were determined.

The experiments recorded with hydrocarbons and their derivatives indicate clearly that a connection exists between surface tension and

chemical constitution, but the data obtained are not yet sufficient to admit of generalisations being made. The author is continuing these investigations. H. C.

Tensions of Vapours. By C. Antoine (*Ann. Chim. Phys.* [6], **22**, 281—288).—In former papers (*Compt. rend.*, **107**, 681, 778, 836), the author has shown that the tensions of vapours could be calculated by the formula $\log H = A - \frac{B}{t + c}$; the object of this communication is simply to modify some of the coefficients previously given, and to show how far the calculated values agree with those determined experimentally. F. S. K.

Elasticity of Gases. By C. Puschl (*Monatsh.*, **13**, 635—646).—Mendeléeff and others have shown that the product pv, which, in general, decreases on compression and increases on expansion, behaves in a precisely opposite manner at low pressures, and on expansion this product, therefore, reaches a maximum and then decreases. On the other hand, the fact that on compression the product reaches a minimum and then increases is well known. It follows from this that there are, ordinarily speaking, two points at which any gas will exactly obey Boyle's law. From experiments of Witkowski and others, it can be shown that the maximum of pv occurs with rising temperature at higher and higher pressures; the minimum, on the other hand, occurring at lower and lower pressures as the temperature rises. It, therefore, follows that at some particular temperature the above pressures for maximum and minimum pv will become the same, and the two points coincide. The point at which this occurs may be called the *symptotic* point. If the temperature be raised beyond this point, pv will no longer give on compression a maximum and a minimum, but only the one point in which both may be supposed to coincide, a thing which is noticed in the case of hydrogen at the ordinary temperature. The author discusses mathematically certain variations in the different properties of gases in the region of the symptotic point. H. C.

Velocity of Etherification. By V. Kistyakoffsky (*J. Russ. Chem. Soc.*, **22**, 474—476).—The author has deduced the constant of velocity for the etherification of organic acids under the influence of inorganic acids, from experiments made in conformity with the following equations—

$$\frac{dx}{dt} = (a - x)k - xk_1,$$

and

$$0 = (a - \xi)k - \xi k_1,$$

in which a denotes the quantity of organic acid taken, x the quantity of ethereal salt formed, t the time, k and k_1 the constants for the formation and decomposition of the ether: ξ is the value of x for which there is equilibrium between the opposing reactions. Large quantities of water and of alcohol were taken in proportion to the quantity of

organic acid, so that these might be assumed to remain constant during the reaction. On integration, the equations give $k = \frac{\xi}{at} \log \frac{\xi}{\xi - x}$, $k_1 = \frac{a - \xi}{at} \log \frac{\xi}{\xi - x}$, from which $k + k_1 = \frac{1}{t} \log \frac{\xi}{\xi - x}$, the most useful form for calculation.

The quantity of inorganic acid used was less than that of the organic acid present. Under these circumstances it was found that the expression $\frac{1}{t} \log \frac{\xi}{\xi - x}$ was, indeed, appreciably constant. The value of the constant thus obtained diminished as the quantity of water present was increased, and was proportional to the electrical conductivity of the solution when one inorganic acid was substituted for another.

The amount of organic acid converted into ethereal salt when equilibrium had taken place, was found to be proportional to the amount of it originally present in the solution. J. W.

Attempt to found a Chemical Theory on a Basis of Physical Comparison. By G. JAUMANN (*Monatsh.*, **13**, 523—566).—This paper contains an attempt to formulate a theory which might take the place of the atomic theory. It is purely inductive in all its parts, and does not start with preconceived ideas as to the constitution of matter or the nature of the change to be observed, but demands only for the explanation of stochiometric phenomena the existence of a simple physical principle, such as holds for all other physical changes, and only such definite conceptions as are necessary for the application of this principle. If in physical structure all substances are alike, their chemical behaviour is determined by the numerical value of a single property on which all chemical properties depend, and which may be called the chemical condition or the *chemial*. Differences in the values of this property are, as the author shows, approximately measurable, and determine the changes which will take place in given substances under certain conditions. Application of the principle to a number of different cases is made in the paper. H. C.

Inorganic Chemistry.

The Relative Densities of Hydrogen and Oxygen. By Lord RAYLEIGH (*Proc. Roy. Soc.*, **50**, 448—463; compare Abstr., 1888, 643; 1890, 330).—The author has made further determinations of the relative densities of hydrogen and oxygen. The gases were prepared by the electrolysis of water, passed over heated copper or copper oxide free from sulphur, and dried by passing over potash and phosphoric anhydride; suspended matter was arrested by a tube packed with glass wool. A vacuous globe was then filled with the gas to be experimented on and weighed. Oxygen was thus found to be 15·882

times as heavy as hydrogen at mean temperature and barometric pressure. The result is probably accurate to 0·0003 of the whole.

W. J. P.

Preparing Silicon and Aluminium Chlorides. By H. N. WARREN (*Chem. News*, **66**, 113—114).—Silicon chloride, mixed with but little ferric chloride and readily purified by redistillation, is obtained by passing chlorine into siliconeisen, containing 15 per cent. of silicon, heated to redness in a tubulated clay retort, and retaining the less volatile ferric chloride in the upper part of a suitable adapter, while the lower part is cooled in a freezing mixture to condense the silicon chloride. By using hydrochloric acid gas instead of chlorine, ferrous chloride, and the more volatile siliconchloroform, $SiHCl_3$, are obtained.

By the action of chlorine on an alloy of iron with 10 per cent. of aluminium, aluminium chloride is produced, which can be purified by distillation from iron borings. When the pulverised alloy is previously mixed with sodium chloride, the passage of chlorine gives rise to the sublimation of aluminium sodium chloride. D. A. L.

Dehydration of Silver Oxide. By M. CAREY LEA (*Amer. Jour. Sci.*, **261**, 249—250).—The author has proved by a series of careful experiments that precipitated silver oxide obstinately retains some water when dried for 40 hours at a temperature of 100°. Even a temperature of 130—135° fails to expel the last traces of moisture. When heated to 160—165°, it becomes anhydrous, but also loses a little oxygen.

The conclusion to be drawn would apparently be that the point at which the last portions of water were driven off was very close to that at which oxygen began to be disengaged; but the author has shown that oxygen is lost long before the last portions of water escape. If silver oxide, after being thoroughly dried at 100°, is moistened with dilute hydrochloric acid, a chloride is obtained of a deep lilac colour, showing the formation of an argentous compound. L. DE K.

Decomposition of Strontium Bromate by Heat. By A. POTILITZIN (*J. Russ. Chem. Soc.*, **22**, 454—469).—Strontium bromate crystallises in monoclinic prisms with 1 mol. H_2O, which it loses at 120°. The anhydrous salt begins to decompose perceptibly at 240° without melting, the decomposition taking place chiefly in two directions, namely, into strontium bromide and oxygen, and into strontium oxide, bromine, and oxygen. The first reaction is the principal one;

Temperature.	Salt taken, gram.	Time for complete decomposition.	Total loss of weight per cent.	SrO formed per cent.
252°	0·802	8 hrs. 15 m.	33·91	5·57
265	0·540	3 „ 10 „	30·52	2·79
269—270°	0·749	1 „ 30 „	28·98	—
271°	0·7895	1 „ 54 „	28·46	0·56
271	0·9855	1 „ 40 „	28·31	—
273	0·7275	1 „ 10 „	28·38	0·55
287	0·5698	0 „ 32 „	28·39	0·52

the extent to which it occurs, however, varying considerably with the temperature.

The table, p. 11, contains a summary of the quantitative results arrived at by the author. J. W.

Action of Silver Oxide on Magnesium Nitrate. By A. KORMILITZIN (*J. Russ. Chem. Soc.*, **22**, 488—492).—Solutions of freshly crystallised magnesium nitrate, $Mg(NO_3)_2 + 6H_2O$, were shaken up in the dark with weighed quantities of freshly precipitated silver oxide. After a given time, the solution was filtered off, and both it and the residue analysed, in order to determine the proportion of silver oxide which had been converted into silver nitrate. The following table contains a summary of the author's results :—

Duration of experiment.	Percentage change with		
	⅓-Normal $Mg(NO_3)_2$.	Normal $Mg(NO_3)_2$.	3-Normal $Mg(NO_3)_2$.
1 day	0·15	0·41	0·51
2 days.....	0·17	0·47	0·54
14 „	0·24	0·68	0·75

The amount of change is thus not proportional to the concentration of the magnesium nitrate solution, although it is so, approximately, when we pass from the ⅓-normal to the normal solution. J. W.

Atomic Weight of Copper. By T. W. RICHARDS (*Chem. News*, **65**, 236—237, 244—245, 260—261, 265—268, 281—282, 293, 302—303; **66**, 7—9, 20—21, 29—31, 47—48, 57—58, 74, 82—83; compare Abstr., 1891, 805).—The atomic weight of copper is deduced from: I. The analysis of cupric sulphate. II. The synthesis of cupric sulphate. III. The analysis of cupric oxide. All calculations are based on the atomic weights: oxygen, 16·000; barium, 137·10; bromine, 79·955; carbon, 12·002; hydrogen, 1·008; silver, 107·930; sodium, 23·053; sulphur, 32·060.

The standard weights used (described in *Proc. Amer. Acad. Arts Sci.*, **25**, 196) were carefully compared with the standards of the Washington Bureau of Weights and Measures. Excepting in the first series of experiments on cupric sulphate, the method of weighing by substitution was used. All weighings were reduced to the vacuum standard.

Full details are given of the methods used in the purification of the materials and reagents employed.

I. Analysis of Cupric Sulphate.—For the first series of analyses the cupric sulphate was coarsely powdered, dried to constant weight over a mixture of crystallised and partially dehydrated cupric sulphate, and the copper determined by electrolysis. The sulphuric acid set free was determined by sodium carbonate and by weighing

the sodium sulphate formed. In the third place, the loss of water at 250° was also determined. The sum of the constituents was 99·87, the water lost at 250° being 35·958 per cent., whereas, if Cu = 63·60 or 63·33, the total water present should be 36·0695 or 36·109 respectively.

In the second series of analyses, the cupric sulphate was dried at 255° in a platinum crucible, and then treated with 20 drops of pure sulphuric acid, and the whole kept at 365° for 3½ hours. There was a further loss of moisture, amounting to 0·108 per cent. of the crystallised sulphate. The dry sulphate was dissolved, and the clear solution electrolysed in a platinum crucible, previously coated inside with copper. After 120 hours, the weak current was interrupted, and the acid rapidly washed into a platinum bottle. Rather less than the required amount of sodium carbonate was weighed out, ignited at a dull-red heat to constant weight, dissolved in water, and added to the acid in the bottle. The very slight excess of acid was titrated with sodium hydroxide, using methyl-orange as indicator. The neutral solution was evaporated, and the residue of sodium sulphate fused and weighed. From the results the following ratios were deduced:—

$Na_2CO_3 : Cu = 106·108 : 63·606$, and $Na_2SO_4 : Cu = 142·166 : 63·595$.

Including the water driven off between 255° and 365°, the sum of the constituents determined reached 99·954.

The third series of analyses was carried out by the same method but with greater refinement. To ascertain whether the method of drying affected the percentage of acid present, the first sample was not dried, the second was only heated at 250°, the third was heated at 365°, after addition of sulphuric acid. The SO_4 found was 38·443, 38·435, and 38·431 per cent. in the three cases.

The fourth experiment of the series was not of the same order of accuracy. The SO_4 was weighed as $BaSO_4$. The adhering barium chloride being estimated and allowed for, this experiment gave SO_4 = 38·434 per cent.

This series gave, as the sum of the constituents determined, 99·951. The deficiency was proved to be due to water still retained at 360°. It was determined by heating to dull redness, and estimating the sulphuric anhydride driven off at the same time. The difference between the loss and the sulphuric anhydride driven off amounted to 0·042 per cent. as a mean of four experiments, varying from 0·019 to 0·055. The final result of these analyses gave:—

Water lost at 360—400°	36·067	per cent.
Water lost between 400° and redness	0·042	,,
Copper	25·449	,,
SO_4	38·436	,,
	99·994	,,

There is an unavoidable excess of water, due to mother liquor enclosed during crystallisation.

Rejecting the ratios including the water of crystallisation, the atomic weight of copper may be calculated as follows:—

Ratio.	Lowest.	Highest.	Experimental mean.
1. $(CuSO_4 - Cu) : Cu$ ..	(63·53)	63·62	63·593
2. $Na_2CO_3 : Cu$	63·592	63·604	63·600
3. $Na_2SO_4 : Cu$	63·59	63·61	63·607
4. $Na_2CO_3 : CuSO_4$	63·61	63·64	63·621
5. $Na_2SO_4 : CuSO_4$	63·59	63·67	63·641
6. $BaSO_4 : Cu$	(63·57)	(63·63)	63·603
7. $BaSO_4 : CuSO_4$	(63·54)	(63·69)	63·625
Average			63·612
Average omitting 5 and 7 ..			63·605

The foregoing experiments furnish data for the calculation of the atomic weight of sulphur. As the average of eight experiments, S = 32·063; omitting three experiments of less value than the remainder, S = 32·075.

II. The Synthesis of Cupric Sulphate.—Cupric sulphate was synthesised from metallic copper and from cupric oxide. Pure electrolytic copper was dissolved by the purest nitric acid in a platinum bottle supplied with bulb tubes to act as a spray condenser. The solution was evaporated with a slight excess of pure sulphuric acid in a platinum dish. The residue was gradually heated to 400°, and cooled in a phosphoric anhydride vacuum desiccator. It was always found to contain free sulphuric acid, and hence no trustworthy results were obtained. The cupric oxide (for preparation see *Proc. Amer. Acad. Arts Sci.*, **25**, 199) was treated in the same manner as the copper. The average percentage of cupric oxide in the sulphate formed was 49·838 (three experiments), as compared with 49·856 if Cu = 63·6. The close agreement is due solely to the effect of opposing errors.

III. The Analysis of Cupric Oxide.—The cupric oxide, when tested by reduction with carbon monoxide, was found to retain no appreciable amount of water at a red heat. It did not contain any carbonic anhydride or any higher oxides or nitrogen oxides. A large number of experiments, in which the cupric oxide, after varied treatment, was entirely dissolved, proved: (1.) That cupric oxide, prepared by ignition of the oxynitrate after Hampe's method, contained between four and five times its volume of occluded gas. (2.) Ignition of this oxide at bright redness expelled a portion of the gas. The temperature of the ignition was apparently higher than that used by Hampe. (3.) Beyond a certain limit, the time of ignition made no important difference. (4.) The gas was not absorbed during cooling. (5.) Specimens of cupric oxide, prepared in different ways, contained very different amounts of gas.

A series of three more carefully carried out experiments on pure cupric oxide, similar to that used in the synthesis of cupric sulphate, gave the percentages of occluded gases as 0·088 nitrogen and 0·004

oxygen. This, applied as a correction to the two best results obtained in the analysis of cupric oxide, gave Cu = 63·605.

The indirect results from the synthesis of cupric sulphate from the oxide, corrected in the same way, gave 63·603.

It is concluded that Hampe's work was subject to serious error, for which it is now impossible to make correction.

A summary of the results obtained by the author between 1887 and 1891 gives, for the atomic weight of copper, general average: (*a*) of 11 series, 63·610; (*b*) of 43 determinations, 63·606. Average of the five most trustworthy series, 63·604. W. T.

Ternary Alloys. Part V. Determination of Various Critical Curves, their Tie Lines and Limiting Points. By C. R. A. WRIGHT (*Proc. Roy. Soc.*, **50**, 372—395; compare Abstr., 1891, 1158).—The author has continued the experiments with mixtures of chloroform, water, and acetic acid, and finds the average composition for the "limiting point" at 18° to be 42·16 per cent. of chloroform, 16·21 of water, and 41·63 of acetic acid. It is noteworthy that the chloroform and water are here present almost in the molecular ratio $2CHCl_3,5H_2O$; this may, however, be merely a coincidence.

The percentages of lead, tin, and zinc contained in a mixture of these metals at 565—570°, at the limiting point, are approximately 22, 35, and 43 respectively, whilst at 750—850° the numbers are 24, 32, and 44. Tables are given showing the composition of the alloys of the metals obtained near 650°; the composition corresponding with the limiting point, as deduced from these, is 22·5, 42·5, and 35·0 per cent. of lead, zinc, and tin, respectively. The tie lines on the critical curve show two maxima, one corresponding with the molecular compound Pb_3Sn, the other to $SnZn_4$. The ratio between lead and zinc at the limiting point approximates to $PbZn_6$ at both 650° and 800°.

The limiting point for an alloy of bismuth, zinc, and tin, at 650°, corresponds with percentages of 18·5, 60·0, and 21·5 of these metals respectively.

For alloys of lead, zinc, and silver at about 800°, the limiting point corresponds to 48·2, 6·3, and 45·5 per cent. of the respective constituents. Lead and zinc are present in the proportion of Pb_2Zn, not $PbZn_6$, as when tin is the solvent. The effect of the formation of the compounds $AgZn_5$ and Ag_4Zn_5 on the critical curve is very marked.

The critical composition at about 750° for alloys of bismuth, zinc, and silver is 33·12, 22·25, and 44·63 per cent. respectively, representing a ratio between bismuth and zinc, approximately indicated by $BiZn_3$; when tin is the solvent metal, the corresponding ratio is nearly represented by $BiZn_{10}$. The formation of the compounds $AgZn_5$ and Ag_4Zn_5 is indicated on this critical curve, just as on that of the lead-zinc-silver alloys. W. J. P.

Certain Points in the Interaction of Potassium Permanganate and Sulphuric Acid. By F. A. GOOCH and E. W. DANNER (*Amer. J. Sci.* [3], **44**, 301—310).—Jones (Trans., 1878, 95), and more recently Brauner, have observed the evolution of oxygen from solu-

tions of potassium permanganate and sulphuric acid during oxidation effected by their means. The authors also find this to be the case, and that the decomposition of the permanganate by the acid increases with the amount of acid present, the time of action, and increase of temperature. A 20 per cent. solution of the acid produces no appreciable effect at ordinary temperatures, and under exposures of a few hours only. In five days, however, a very considerable action takes place at the ordinary temperature, and heating the mixture of acid and permanganate to 80° for an hour and a half is closely comparable in its effect with that brought about by the five days' action at the ordinary temperature.

It appears, from further experiments, that the change is brought about by a tendency towards reduction on the part of the acid. When the acid is not present in proportion greater than 50 per cent. of the mixture, in the early stages of the action the oxygen lost by the permanganate is liberated, but later on the decomposition of the permanganate results in the precipitation of manganese in the form of a higher oxide, or in the retention of the manganese in solution in the form of a higher sulphate. H. C.

The Passive State of Iron and Steel. Part III. By T. Andrews (*Proc. Roy. Soc.*, **49**, 481—488; compare Abstr., 1891, 250).—Considerable differences are to be observed between the relative passivities of wrought iron and hard and soft cast steels, Bessemer steels and Siemens steels; variations in the chemical composition and physical structure of the metals greatly influence the passive state. Wrought iron was found to be less passive than the steels employed, being electropositive to them when placed in nitric acid; the difference of potential established between the two metals was in some cases as much as 0·1 volt. In some instances the wrought iron did not become electropositive until immersed for 2 to 3 hours in the acid; the difference in potential then gradually increased, showing that the wrought iron was slowly becoming less positive than the steel. Wrought iron is electronegative to tungsten steel, and is hence more passive than the metal. The E.M.F. developed in circuit between wrought iron and soft steels containing but little combined carbon, when immersed in cold nitric acid (sp. gr. 1·42), is much less than that developed with hard steels containing more combined carbon. Steels containing a high percentage of combined carbon are more passive than those containing a smaller quantity. W. J. P.

Action of Nitric Acid on Potassium Dichromate. By G. C. Schmidt (*Ber.*, **25**, 2917—2918).—In 1871, Darmstädter described the formation of two crystalline compounds, $Cr_2O_5(OK)NO_2$ and $Cr_3O_8(OK)NO_2$, by the action of nitric acid on potassium dichromate (this Journ., 1871, 199). The author, repeating Darmstädter's experiments, obtained potassium tetrachromate, $K_2Cr_4O_{13}$, but was unable in any way to obtain a compound containing nitrogen. The substances Darmstädter obtained were undoubtedly mixtures of the tetrachromate with potassium nitrate. L. T. T.

Ammonium Chromates. By E. Maumené (*Bull. Soc. Chim.* [3], **7**, 174—179).—Concentrated aqueous chromic acid or potassium dichromate, when neutralised by ammonia, deposits ammonium chromate, $(NH_4)_2CrO_4$, in yellow, crystalline tufts, which resemble those of the potassium salt, but soon lose ammonia, and change into the dichromate. The salt is best crystallised by evaporating the slightly ammoniacal solution over quicklime, and should be kept in sealed vessels.

Ammonium chromate yields a brown oxide, CrO_2, when heated at 204°, identical with the oxide which was described by Vauquelin as precipitated on heating the aqueous solution, although in all probability it is formed only on the superheated sides of the vessel. When the temperature is raised to 220—225°, explosive decomposition occurs, and the oxide CrO is formed, which, however, takes fire at once, and burns to the green oxide Cr_2O_3; it is probable that the compound $N_2H_4CrO_3$ is formed as an intermediate product. The brown oxide is soluble in aqueous chromic acid or alkaline dichromates, forming brown solutions, from which it is reprecipitated by excess of water.

The deliquescent, crystalline, double chromate of ammonium and potassium, $(NH_4)_2CrO_4,K_2CrO_4$, prepared by dissolving potassium dichromate in concentrated aqueous ammonia, and evaporating the yellow, syrupy solution over quicklime, turns brown at 240°, owing probably to the formation of the chromate of a base N_2H_6O, and is completely decomposed at 270°, the green oxide Cr_2O_3 remaining.

Jn. W.

Preparation of Vanadyl Trichloride: Extraction of Vanadium from its Ores. By L. L'Hôte (*Ann. Chim. Phys.* [6], **22**, 407—412).—For the extraction of vanadium from its ores the author takes advantage of the volatility of vanadyl trichloride. The finely divided mineral is intimately mixed with about one-quarter of its weight of lamp-black and a little oil, and ignited to volatilise the arsenic and zinc; the calcined product is then slowly heated to 300° in a stream of dry chlorine, and the vanadyl trichloride collected in tubes immersed in a freezing mixture.

When it is desired to determine the quantity of vanadium in an ore, the above method is employed, and the vanadyl trichloride is collected in a series of bulbs containing distilled water; the vanadic acid is then reduced with zinc, and estimated volumetrically with the aid of potassium permanganate.

Samples of bauxite, examined in this way, were found to contain 0·03 to 0·05 gram of vanadium per kilo.; two samples of pitchblende from Bohemia contained 1·62 and 1·40 grams of vanadium per kilo. respectively.

F. S. K.

Refining Gold, Silver, and Platinum. By H. N. Warren (*Chem. News*, **66**, 140—141).—Gold is separated from its alloys by melting them with 2½ times their weight of silver, then parting with nitric acid; the silver being subsequently precipitated by copper and the latter metal by iron. By treating silver platinum alloys with nitric acid, all the former and all or part of the latter metal are dissolved; but by precipitating both metals from this solution by copper,

and again treating the precipitate with nitric acid, the silver only is dissolved. D. A. L.

Mineralogical Chemistry.

Beyrichite from Altenkirchen. By H. Laspeyres (*Zeit. Kryst. Min.*, **20**, 535—550).—An examination of this very rare mineral from the Lammerichskaule mine, at Altenkirchen, in the Siegen district, has, in the main, confirmed the results published by Liebe in 1871. Beyrichite bears the same relationship to millerite that augite does to uralite. Beyrichite is the mother mineral from which millerite has been formed by a rearrangement of the molecules. Both minerals have the same crystalline form and composition, but different physical properties. Analysis of beyrichite gave results in accord with the formula (NiCoFe)S. B. H. B.

Cobaltiferous and Nickeliferous Iron Pyrites from Müsen. By H. Laspeyres (*Zeit. Kryst. Min.*, **20**, 553—555).—The crystals examined by the author occurred in a fissure in brown spar at the Heinrichssegen mine, at Müsen. Analysis gave the following results:—

S.	Fe.	Co.	Ni.	Total.
51·35	42·68	1·97	4·13	100·13

The mineral appears to consist of a crystal of iron pyrites covered by a parallel deposition of polydymite crystals on its surface. B. H. B.

Pseudobrookite, Hæmatite, and Anhydrite as Sublimation Products. By B. Doss (*Zeit. Kryst. Min.*, **20**, 566—587).—The author describes the occurrence of pseudobrookite, hæmatite, and anhydrite as sublimation products in the furnaces of the Hermania soda works at Schönebeck. Numerous other minerals of recent formation have previously been found at the same works, the list including: (1) specular iron ore, (2) magnetite, (3) iron pyrites, (4) magnetic pyrites, (5) a tetragonal calcium aluminium silicate isomorphous with gehlenite, (6) a calcium silicate, (7) crystallised lime, (8) glauberite, (9) gaylussite, (10) rhombic silico-carbonate, and (11) octahedral crystals of sodium fluorophosphate ($NaF,2Na_2PO_4 + 18H_2O$), with 1·2 to 1·3 per cent. of vanadic acid. Pseudobrookite has not hitherto been found as a sublimation product in technical working. The analysis of the Schönebeck product gave results in accord with the formula Fe_2TiO_5. B. H. B.

Soda from the Alkaline Waters of Owen's Lake. By E. Le Neve Foster (*Zeit. Kryst. Min.*, **20**, 631; from *Proc. Colorado Sci. Soc.*, **3**, 245—254).—The author describes the manner in which soda is obtained from the highly alkaline water of Owen's Lake in Myo Co., California. The lake, which is at an altitude of some 3,600 feet, lies in a basin apparently of volcanic origin between the Sierra Nevada

and the Myo chain of mountains. The lake has no outlet and its chief feeder is the Owen's River, coming in from the north. The composition of the water is as follows:—

SiO_2.	$MgCO_3$.	KCl.	NaCl.	Na_2SO_4.	$Na_4B_2O_7$.	Na_2CO_3.
0·220	0·055	3·137	29·415	11·080	0·475	26·963

$HNaCO_3$.	Al_2O_3,Fe_2O_3.	Total.
5·715	0·038	77·098

The water of Lake Albert contains 39·172, Mono Lake 53·473, and Lake Bagtown 129·01 of solids per litre. The water is pumped into reservoirs, and the soda obtained by evaporation. In 1889, in this way 1,000 tons of soda was obtained, and in 1890 double that amount. B. H. B.

Synthesis of Minerals of the Hauyn Group. By J. Morozie-wicz (*Jahrb. f. Min.*, 1892, ii, Mem. 139—141).—It has been shown by Lemberg that hauyn and sodalite, at an intense heat, lose sulphuric acid and chlorine respectively. For this reason, it has been found impossible to prepare these minerals artificially in a crystalline state. The results of the author's experiments on the synthesis of hauyn are as follows:—1. A mixture of 65 parts of $SiO_2,3H_2O$ with 44 parts of $Al_2O_3,3H_2O$ and 33 parts of gypsum was heated for 6 hours in an excess of Glauber's salt in a platinum crucible. The melted mass was treated with cold distilled water, filtered, and washed until the filtrate gave no precipitate with barium hydroxide. The resulting product, an infusible, greyish powder, was found under the microscope to contain crystals of hauyn. 2. The same mixture treated with molten sodium sulphate and sodium chloride gave some very fine and regular crystals, together with columnar twin crystals of sodalite. 3. The same mixture inserted in sodium chloride alone gave crystals apparently consisting of pure sodalite. The author is continuing his experiments with a view of attaining further information regarding the processes obtaining in the formation of hauyn and sodalite in lava. B. H. B.

The Chlorite Group. By G. Tschermak and E. Ludwig (*Jahrb. f. Min.*, 1892, ii, Ref. 227—232; from *Min. petr. Mitth.*, **12**, 32—39).—Numerous analyses are given in support of Tschermak's theory that the chemical structure of the chlorites may be explained by dividing this group of minerals into two sub-groups, orthochlorites and leptochlorites. The orthochlorites are believed to be mixtures of two end products, serpentine and amesite; whilst, for the leptochlorites four other fundamental compounds are assumed, strigovite, chloritoïd, and two derivatives of amesite. Representing these minerals by symbols, the chlorites may be classed as follows:—

A. *Orthochlorites.*—Pennine, Sp_3At_2; clinochlore, SpAt; prochlorite, Sp_3At_2 to Sp_3At_7; corundophilite, Sp_3At_2 to $SpAt_4$; amesite, $SpAt_4$ to At.

B. *Leptochlorites.*—I. Daphnite, $(At'At)_3Sp_4$; chamoisite, $(At'At)_3Sp_4$. II. Metachlorite, $(StAt_3)_2Sp_3$; clementite, $(StAt_2)_2Sp$; cronstedtite StAt; euralite, St_4At_3 (strigovite = St). III. Diabantite, Ct_4Sp_7

aphrosiderite, $(CtAt)_6Sp_4$; delessite, $(CtAt)_2Sp_5$ to CtSp; rumfite, $(CtAt'')_4Sp$ (chloritoïd = Ct).

C. *Mixed Alteration Products.*—Tabergite, pyrosklerite, loganite, pseudophite, vermiculite, hallite, berlauite, enophite.

D. *Chlorites not yet Defined.*—Epichlorite, grengesite, melanolith.

B. H. B.

Meteoric Iron. By E. Cohen and E. Weinschenk (*Jahrb. f. Min.*, 1892, ii, Ref. 244—246; from *Annalen des k.k. Naturhistorischen Hofmuseums*, **6**, 131—165).—The authors have endeavoured to solve a number of problems connected with meteoric iron.

1. Cohenite seems to be confined to the Arva group. The composition of cohenite from the Magura meteoric iron is in accord with the formula $(FeNiCo)_3C$, whilst that of the iron carbide from the Wichita meteoric iron is in accord with the formula $(FeNiCo)_4C$.

2. The composition of schreibersite is in many cases constant in that the ratio of Fe + Ni + Co to P is fixed; its formula being $(FeNiCo)_3P$. The new analyses of schreibersite from the Toluca, Glorieta Mountain, and Hraschina meteorites confirm this view.

3. The theory propounded by E. Cohen that the hexahedral iron (kamazite) has a constant composition (about 7 per cent. Ni + Co) is supported by the analysis of the meteoric iron from the Hex River Mountains, Cape Colony. The mean composition of kamazite corresponds with the formula $Fe_{14}Ni$.

4. Two varieties of tænite occur in meteoric iron. One is tin-white, flexible, rich in Ni + Co, and contains no appreciable quantity of carbon. To this class belongs the tænite from the Toluca, the Wichita, and the Glorieta Mountain meteorites. The second variety presents a more greyish colour, less lustre, less flexibility, and less nickel and cobalt, whilst carbon is present in appreciable quantities. To this class belongs the tænite from the Staunton and Magura meteorites.

B. H. B.

Physiological Chemistry.

Absorption of Oxygen and Formation of Carbonic Anhydride in Human Respiration. By W. Marcet (*Proc. Roy. Soc.*, **50**, 58—75; compare Abstr., 1891, 1270).—From experiments made on two healthy persons, one 63 and the other 21 years of age, the author arrives at the following conclusions:—(1.) The percentage of carbonic anhydride, oxygen, or nitrogen in the air expired alters with the person experimented on, but the proportion of each gas varies but slightly up to a period of about $4\frac{1}{2}$ hours after the midday meal. (2.) The mean ratio between the oxygen consumed and the carbonic anhydride exhaled is 0·871. (3.) The mean volume of oxygen absorbed per minute is 34·3 c.c. (4.) The mean volume of oxygen absorbed is 0·75 per cent. of the air inspired, and was nearly the same with both subjects. 3·63 per cent. of the oxygen inhaled was absorbed. (5.) The mean weight of oxygen consumed per hour by the older man was 0·355 gram per kilo. of body weight; the weight

absorbed by the younger man was 0·380 gram. (6.) The weight of carbonic anhydride expired was notably greater in the younger than in the older man, and corresponded approximately with the greater consumption of oxygen by the former.

The following results were obtained from an investigation into the respiration of air containing 2·5—4 per cent. of carbonic anhydride:—(1.) The proportion of oxygen in the air expired is slightly greater than in ordinary breathing. (2.) The mean ratio of oxygen absorbed and the carbonic anhydride expired is small, being 0·654 and 0·567 for the older and younger man respectively, as against a mean of 0·871 in ordinary breathing. (3.) The volume of oxygen absorbed is 3—4 times as great as in ordinary breathing. (4.) The proportion of oxygen absorbed from the air inspired is about twice as great as when pure air is breathed. (5.) The weight of oxygen consumed by the body undergoes an increase of about 20 per cent. (6.) The total weight of carbonic anhydride expired is reduced by about 12 per cent. When such air is breathed, therefore, a considerable amount of oxygen must remain in the blood to be transformed into an excess of carbonic anhydride in addition to the proportion required for the other functions of the body. W. J. P.

Action of Fatiguing Muscular Work on the Respiratory Interchange. By A. Loewy (*Pflüger's Archiv*, **49**, 405—422).—During ordinary muscular activity the combustion processes in the body take the same direction as during rest; this is shown by the respiratory quotient remaining constant. When the work becomes excessive, this normal is upset and the respiratory quotient rises. The muscular katabolism is not directly dependent on the work actually performed, but on the amount of muscular energy expended; this is a variable quantity, as under favourable conditions muscle works more economically (that is, with a less loss of heat) than when the conditions are unfavourable; one of the unfavourable conditions is fatigue. In other words, during fatigue more muscular activity is expended in doing a given amount of work, than when the muscle is fresh. At the end of a period of work the respiratory processes remain increased for a few minutes; if, however, fatigue has supervened, or the work has been done under unfavourable conditions (for instance, with an insufficient supply of oxygen), the respiratory exchanges remain disturbed for a longer period. W. D. H.

Influence of Acetic Acid on Gaseous Metabolism. By A. Mallèvre (*Pflüger's Archiv*, **49**, 460—477).—When cellulose is ingested, it undergoes certain putrefactive changes leading to the formation of carbonic anhydride, methane, acetic, and butyric acids. In estimating the nutritive value of cellulose, it is therefore important that we should know the effect which these fatty acids have on metabolism. The present experiments were made on rabbits, and chiefly with acetic acid, which was intravenously injected as sodium acetate. It was found that the quantity of oxygen used by the animal was increased during and after the injection and that the carbonic an-

hydride produced fell relatively; the respiratory quotient was consequently lower; in four experiments the R.Q. was as follows:—

	1.	2.	3.	4.
Before injection.....	1·04	0·77	0·77	0·87
During injection	0·86	0·71	0·69	0·80
After injection	0·76	0·77	0·77	0·79

Other changes noted were increased alkalinity of urine and of the blood, due, doubtless, to the conversion of acetate into carbonate.

The sinking of the respiratory quotient shows that some acetic acid was burnt up; the theoretical R.Q. of acetic acid is 0·5. The R.Q. found never sank so low as this, showing that other materials in the body were being simultaneously oxidised. It is, however, considered that any sparing action exercised by the acetic acid formed from cellulose would be more than counterbalanced by the increased work thrown on the digestive organs, and a consequent larger necessary supply of oxygen.

Nutritive Value of Cellulose. By N. Zuntz (*Pfluger's Archiv*, **49**, 477—483).—This paper consists of remarks of a general nature on the foregoing, and a critical review of those researches which have attempted to show that cellulose has any great nutritive value.

W. D. H.

Researches on Blood. By L. Lilienfeld (*Chem. Centr.*, 1892, ii, 82—83; from *Arch. Physiol.*, 1892, 115—154).—The small plates which, besides the red and white corpuscles, exist in the blood have been examined by treating them with an artificial digestive fluid; they were found to consist of a granular portion, nucleïn, and a homogeneous portion, chiefly albumin. The nucleïn is separated out by the pepsin ferment from its compound with albumin which exists in the plates, and can then be identified by its chemical reactions. C. F. B.

Some Results of Transfusion. By H. C. Geelmuyden (*Arch. Anat. und Physiol., physiol. Abth.*, 1892, 480—496).—If a large quantity of living blood is introduced into the vascular system of a dog, the animal remains healthy. Its excretion of nitrogen is, however, increased for several days. The increase is not from excess of proteïd food, and the body weight does not fall. The increase of nitrogen can be accounted for by the excess of nitrogenous matter introduced into the blood. The increase lasts as long as the increase in the blood constituents does; when this reaches a maximum, the new blood is katabolised and the animal, as regards both blood and nitrogenous output, returns to the normal. Extravasation of blood is never found. The opinion is expressed that the seat of the destruction of the corpuscles is the blood stream itself. There is, however, no solution of the hæmoglobin from the corpuscles; not once was the serum found to be red. W. D. H.

Pancreatic Juice in Different Animals. By V. D. Harris and W. J. Gow (*J. Physiol.*, **13**, 469—492).—From the examination of the

ferments of the pancreas in a large number of animals, the tryptic ferment was far the most constantly present and the more resistant; then the rennetic, and then the diastatic. The fat splitting ferment is often absent, and it is always readily destroyed, for instance, by preserving the pancreas in alcohol. No special fat-emulsifying agent was ever found. Of the animals examined, four only (man, pig, ox, sea-eagle) were in the first class as regards the activities of all their pancreatic ferments.

A few experiments with pancreases removed from individuals who had died of wasting disease showed that the activity of the ferments was much diminished.

In pig's pancreas, no inversive ferment was found. Fresh pig's pancreas, however, converts raw starch into dextrin, but not into dextrose. The diastatic action on cooked starch was not hindered by the presence of phenol (1 in 130) or of mercuric chloride (1 in 1000).

W. D. H.

Conversion of Maltose into Dextrose. By L. E. Shore and M. C. Tebb (*Proc. Physiol. Soc.*, 1892, 19—20).—Various organs (intestinal wall, pancreas, lymphoid structures) were dried at a low temperature and added to solutions of maltose. The largest change was obtained with the intestinal mucous membrane from the pig. After 21 hours' action in the warm bath, the sugars present were 19 per cent. maltose, and 81 per cent. dextrose. In another experiment (the mucous membrane being freed from Peyer's patches), the numbers were 35·3 and 64·7 respectively. The Peyer's patches gave 63·3 and 36·7. Brown and Heron found, on the contrary, that lymphoid tissue was more active than ordinary mucous membrane. In the present research, lymphatic gland gave 72 and 28. With pancreas, the action was still less, 76 and 24. Pancreatic extracts gave only a trace of dextrose after 24 hours.

The experiments show that the change of maltose into dextrose is not accomplished by the pancreas but by the intestine, and, further, not so much by the lymphoid tissue as by the mucous membrane of the gut; but whether it is effected by the secretion poured out into the intestinal cavity, or by the cells through which the solutions pass during absorption, is not indicated by these experiments.

W. D. H.

Fluorine Compounds in the Organism. By J. Brandl and H. Tappeiner (*Zeit. Biol.*, **27**, 518—539).—Experiments on dogs which were fed on food admixed with sodium fluoride show that the soluble fluorine compound administered causes an increase in the amount of that element in the body. A great part is deposited in the bones in the form of a crystalline compound, which probably is identical with fluor-spar.

W. D. H.

Absorption of Iron. By A J. Kunkel (*Pfluger's Archiv*, **50**, 1—24).—The present experiments on animals show that small quantities of iron are absorbed when that metal is administered in the form of inorganic salts. It appears to collect in the liver. It is possible that these substances may be changed in the intestine into something like Bunge's hæmatogen before absorption. These hæma-

togenous substances appear to be ill-defined at present as chemical units, and it is probable that the organic iron compounds in various foods are not all identical. W. D. H.

Demonstration of the Presence of Iron in Chromatin by Microchemical Methods. By A. B. MACALLUM (*Proc. Roy. Soc.*, **50**, 277—286).—The presence of iron in the chromatin of cellular elements of such tissues as are almost free from hæmatin may be proved by running a drop of freshly prepared ammonium sulphide on to the fresh section; a cover glass is then placed on the latter and the edges sealed with glycerol. On maintaining the preparation at a temperature of 60° for some days, the chromatin nodules become stained light green to black, thus proving the presence of iron. Albuminate iron or inorganic iron compounds may be previously removed, if necessary, by treatment with Bunge's fluid.

Iron was found in the chromatin of the cells of numerous organs and tissues of *Necturus*, *Oniscus*, and various placentæ. It is also present in the chromatin of the pollen cells of *Dianthus*, *Cucurbita*, *Narcissus*, and *Hyacinthus*, and in the gonidia of *Cystopus candidus*. W. J. P.

Absorption of Fats. By O. FRANK (*Arch. Anat. und Physiol., physiol. Abth.*, 1892, 497—512).—In some experiments on dogs, analysis of the intestinal contents shows that, when the thoracic duct is ligatured, a very large absorption of the fatty acids from the fat in the food goes on. A few analyses of the blood were performed, but these appear to be insufficient for purposes of comparison. Most, however, show a rise in the percentage of fat and lecithin as compared with the normal. Soaps and cholesterol are apparently unaltered in quantity. W. D. H.

Nutritive Value of Alcohol. By F. STRASSMANN (*Pflüger's Archiv*, **49**, 315—330).—The statement of Bödlander (*ibid.*, **32**) that 95 per cent. of the alcohol taken under ordinary conditions is used by the organism should be amended; the correct number is 90 per cent. Without entering into the question of the therapeutic value of alcohol, it is thus seen that it is a nutritive agent. There are, however, many other substances with the same or even greater nutritive value, without the poisonous action of alcohol. W. D. H.

Digestibility and Nutritive Value of Bread. By N. ZUNTZ and A. MAGNUS-LEVY (*Pflüger's Archiv*, **49**, 438—460).—In men not doing excessive mechanical work, more than half of the oxygen used up is consumed in muscular activity.

A diet very poor in proteïd is well assimilated by the human digestive tract; and addition of starch to bread does not impair its nutritive value. One must not, however, go too far in the restriction of proteïd. No injurious influence was observed by the addition of 60 grams of alcohol.

During feeding on white bread and butter, the digestive work requires at least 10 per cent. more oxygen than when the digestive

organs are at rest; and more than 5 per cent. of the nutriment given is consumed in the assimilation of food. W. D. H.

Formation of Sugar in the Liver. By J. SEEGEN (*Chem. Centr.*, 1892, ii, 84; from *Arch. Physiol.*, 1892, 34—53).—A reply to Pflüger (*Chem. Centr.*, 1891, ii, 713, and 1892, i, 37), upholding the author's view that sugar is produced by the normal action of the liver. He thinks that the proteïds contained in nitrogenous food are completely decomposed in this organ, the nitrogen being converted into carbamide, and the carbon into sugar, the latter, in his opinion, being the source of all the energy of the animal body. C. F. B.

Deposition of Albumin during the Fattening of Full Grown Animals. By T. PFEIFFER and G. KALB (*Bied. Centr.*, **21**, 579—588; from *Landw. Jahrb.*, 1892, 175—203).—The object of the experiments was to ascertain whether there is a continuous deposition of albumin during a long period of fattening (about 100 days). There were two experiments, each with two full grown, lean sheep (weighing about 42 and 35 kilos.). In the one experiment, the sheep (Nos. 1 and 2) had each day:—hay (500 grams), salt (10 grams), crushed beans (400 grams), and earth-nut cake (200 grams); in the other experiment (sheep 3 and 4) the same amounts of hay and salt were given with crushed beans (200 grams) and crushed barley (320 grams). The amount of water consumed was determined daily. The amount and composition of the excrement, and from this the amounts of food constituents digested, were determined at the beginning, in the middle, and at the end of the experiment. The results are given in tables. It is shown that, as the fattening progresses, there is generally no very considerable difference observed in the digestibility of the food, but the following table shows that the digestion coefficients did fall somewhat:—

	Sheep No. 1.	Sheep No. 2.	Sheep No. 3.	Sheep No. 4.
1st period	76·14	75·53	75·06	72·14
2nd period	71·75	74·17	72·81	72·76
3rd period	74·46	74·45	72·21	69·42

The albumin of the food in Experiment 1 was more completely digested than that of Experiment 2. In the digestibility of the ether extracts there were great differences, owing, the author thinks, to the presence of soluble substances in the fæces produced by fermentation in the intestines. To overcome this difficulty, separate determinations of fat, free fatty acids, and other substances soluble in ether should be made; but experiments hitherto made in this direction gave only negative results.

The decomposition of albumin remained fairly constant in the three periods of Experiment 1, but in Experiment 2, there was an unmistakable rise in the second and third periods as compared with the first. The results are, however, somewhat affected by the consumption of water being insufficient in the case of sheep 1, 2, and 3. It is pointed out that an insufficiency of water may give rise to totally

reversed results, so that in experiments with animals, there should be no restraint as regards amount of water.

A table is given, showing the nitrogen balance in grams per day. When the amount of nitrogen in the increase of wool (which is estimated as 0·89 gram per day) is deducted from the total gain of nitrogen, the following numbers are obtained, indicating the amount of nitrogen deposited in the form of flesh :—

	Sheep 1.		Sheep 2.	
	Gram.	Per cent. of digested N.	Gram.	Per cent. of digested N.
1st period	1·29	3·91	1·15	3·51
2nd period	0·71	2·17	0·74	2·32
3rd period	0·73	2·26	1·21	3·74

	Sheep 3.		Sheep 4.	
	Gram.	Per cent. of digested N.	Gram.	Per cent. of digested N.
1st period	2·06	9·84	1·71	8·63
2nd period	—	—	—	—
3rd period	—	—	—	—

Apart from wool production, there was in the second period in Experiment II a complete nitrogen equilibrium, whilst, at the commencement, there was a daily gain of 1·88 gram of nitrogen, corresponding with 55 grams of flesh. In Experiment I with the lower nutritive ratio (1 : 2·3), there was a continuous deposition of nitrogen in the form of flesh. The experiments thus confirm the known fact that full-grown animals, fattened in the usual manner, very soon attain a nitrogen equilibrium as regards flesh; they also show that a continued slight production of flesh may occur with food richer in proteïds. This was already observed by Maercker.

	Expt. 1.	Expt. 2.	Excess of Expt. 1 over Expt. 2.
Digested crude protein	202·44	123·11	79·33
„ ether extract	20·05	8·86	11·19
„ crude fibre	100·43	90·67	9·76
„ non-nitrogenous extract	325·42	420·61	−95·19
Increase of live weight	71·5	62·5	9·0

The preceding table shows the average daily amounts of digested food compared with the average increase of live weight.

With regard to the observation that change of nitrogen increases after shearing and then gradually diminishes, it is remarked that experiments should not be commenced directly after shearing, but that the gradual increase in the amount of wool has no appreciable effect on the change of nitrogen. The loss of the wool seems to diminish somewhat the separation of nitrogen. N. H. M.

Chemistry of the Kidney Substance. By L. Liebermann (*Pflüger's Archiv*, **50**, 55—56).—A very large proteïd constituent of the kidney substance is one similar to that found in the gastric mucous membrane, namely, a compound of lecithin and albumin, to which the term lecithalbumin is applied. It may be obtained as a residue after gastric digestion, and is stated to be acid in reaction. W. D. H.

Asparagine as a Nutritive Substance. By G. Politis (*Zeit. Biol.*, **27**, 492—506).—From experiments on rats, the following conclusions are drawn :—

1. A mixture of proteïd, fat, starch, and meat extract either with or without the addition of asparagine will keep the animals in a condition of equilibrium, or even increase the body weight.
2. Fat, starch, and meat extract alone soon produce death; addition of asparagine does not alter this result.
3. Asparagine has no influence on nitrogenous metabolism.

W. D. H.

Physiological Action of Asparagine. By J. Mauthner (*Zeit. Biol.*, **27**, 507—517).—Experiments on dogs show that asparagine acts as a "proteïd-sparing" food in the same way as fats and carbohydrates may. There is, however, no evidence that it exercises this function from the synthesis of proteïd matter from the carbohydrate and asparagine given. W. D. H.

Influence of Sugar on the Constitution of Milk Fat. By A. Mayer (*Bied. Centr.*, **21**, 652—653; from *Milchzeit.*, 1892, 49).—The author recently brought forward the view that the composition of milk fat depends on the feeding, the greatest influence being shown by the soluble carbohydrates. In order to obtain experimental evidence, a six-year-old cow, which had calved about seven months previously, was fed for the week before the commencement of the experiments with the usual winter food, hay with linseed cake (2 kilos.). During the first period (November 17—26) and the third period (December 7—17), beet diffusion chips (32 kilos.), rye straw (5 kilos.), and linseed cake (4 kilos.) was given; in the second period (November 26—December 6), cane sugar (2 kilos.) in addition. The daily yield of milk was 11¼ litres (first period), 12¼ litres (second period), and 10½ litres (third period). A table is given showing the melting point, solidifying point, and the amount of volatile acids in the butter in six different periods. The melting point was lowered by the use of sugar, and rose again in the third period. The amount of volatile acids rose during the second period (with sugar), but was

scarcely diminished at all in the third period. The influence of the sugar on the melting point of the solid fatty acids, separated by Reichert's method, is shown in the table:—

	1st period.	2nd period.	3rd period.
Melting point.....	43·7—43·8	41·4—41·7	42·3—42·4
Solidifying point..	37·6—37·7	35·3	36·5

The results explain the less consistency of Friesland butter as compared with Danish. N. H. M.

Melting Point and Composition of Butter from Cows variously fed. By A. Mayer (*Landw. Versuchs-Stat.*, **41**, 15—35; compare Abstr., 1889, 173).—In the two series of experiments now described, one cow was used in each case. The feeding was changed every two weeks or less, and the sp. gr. and dry matter of the mixed morning and evening's milk determined, the fat being calculated by means of the Fleischmann-Morgen formula; the amount of volatile acids in the butter and the melting and solidifying points of the butter were also determined. These determinations were made 8—10 days after the commencement of each change of feeding, and again two days later. The daily yield of milk was also noted. The volatile acids of the butter varied with the first cow from 13·4 to 24·9; with the second cow from 20·1 to 32·2. The differences are less than those obtained in the earlier experiments, but are still considerable. When the differences of race, of individuals, and also differences in the period of lactation are combined with varying food, the extremes will differ still more widely. With regard to the bearing of this on the judgment of the adulteration of butter from the amount of volatile acids present, it is pointed out that the minimum number allowed for volatile acids is too high for some cases. On the other hand, the lower this number is fixed, the more adulterated butter will be passed over as pure. The only satisfactory manner of detecting adulteration will be to employ a combination of several methods.

The results show, in accordance with those of Nilson, that the period of lactation has some influence on the amount of volatile acids, higher numbers being obtained in the early periods than in the later ones. With regard to the relative effect of the different foods, the greatest depression was found in the case of poppy cake. Meadow grass in spring gave an increase when compared with the results obtained with hay and linseed cake, whilst autumn grass did not produce this effect, probably from its greater similarity to hay. Straw (pea and rye), instead of hay (in conjunction with linseed cake), caused a lowering of the acids from 24 to 16. Sour hay also caused a lowering in the amount of acids. The presence of lactic acid or volatile fatty acids in the food had no apparent action, at least in the small amounts employed. With regard to the manner in which the various foods act on the constitution, it frequently happened that a low amount of volatile fatty acids was obtained when the nutritive ratio of the food was low, and *vice versâ*, but this was not always the

case. It was generally found that the amount of acids varied with the amount of carbohydrates supplied, the greatest quantity of volatile acids being produced when the amount of carbohydrates, especially soluble carbohydrates, given in the food was greatest: thus beetroot was more favourable than hay, hay more favourable than sour fodder, for the production of volatile acids.

The melting and solidifying points of the butter do not always go together; the melting points fall as the period of lactation proceeds, whilst the solidifying points do not show this. Taking, however, the mean of the two temperatures in each case, the period of lactation has but little influence, whilst differences of race and individual show distinctly. As to the effect of different foods, it was found that pea straw and poppy cake taken together give high melting butter; next come straw and linseed or sesame cake, then earth-nut cake, and then cotton cake or rye. Soft butters, as compared with that obtained with the normal ration (hay and linseed cake), are produced by fresh meadow grass. Sour grass behaves in this respect much like hay. The addition of lactic or volatile fatty acids to the food somewhat lowered the melting point of the butter.

When the various foods are arranged in order showing the effect (1) on the amount of volatile acids, and (2) on the melting point of the butter, it is seen that those foods which produce the most acids generally produce the softest butter; but the rule is not without exceptions. N. H. M.

Composition of Over-ripe Cheese. By A. Maggiora (*Exper. Stat. Record*, **4**, 98—99; from *Arch. Hygiene*, **14**, 216—224).—Three samples of gorgonzola were examined: No. 1 was soft and lardy, with an extensive growth of *Penicillium glaucum*, and contained a few maggots, and a greyish, soft liquid mass in the pores. No. 2 was very much changed, was viscous in many places, and had large numbers of maggots. No. 3 had been kept for about seven months in a stoppered bottle after it had become ripe; it was dark yellow, soft, viscous, and had a strong, caustic taste. When examined with the microscope, it was found that as the over-ripeness increased, the number of fat globules diminished, crystals of fatty acids, leucine, and tyrosine became numerous, and the number of bacteria, fungi, and insect eggs, &c., increased very materially. The following analytical results are given in percentages:—

	Dry matter.	Fat.	Total nitrogen.	Proteïd nitrogen.	Amide nitrogen.	Nitrogen as ammonia.	Crude protein.	Proteïds.	Ash less NaCl.	NaCl.
1...	65·59	37·52	4·28	2·59	1·01	0·68	26·75	16·20	2·74	1·33
2...	67·57	34·08	4·15	1·27	1·49	1·26	25·94	7·96	5·78	0·99
3...	62·37	36·19	4·31	0·58	1·88	1·86	26·94	3·63	9·55	0·92

The decomposition of the cheese is accompanied by the production of fatty acids from the fat and of amides and ammonia from the proteïds (paracaseïn). The cheese thus loses its nutritive properties until it may finally become mainly an aqueous solution of fatty acids (free or as ammonium salts), leucine, tyrosine, mineral salts, and a mass of bacteria and fungi. N. H. M.

The Phosphates of Horse's Urine. By L. LIEBERMANN (*Pflüger's Archiv*, **50**, 57—66).—The investigation relates to the phosphates normally present in horse's urine, and the changes that occur after excitation of the central nervous system by coitus, and in certain diseases of the spinal cord in these animals.

As the mean of nine observations on normal animals, the following numbers are obtained :—

Quantity of urine in 24 hours	3331 c.c.
Specific gravity	1·047
Total quantity of P_2O_5 in 24 hours...	0·2867 gram.
Percentage of P_2O_5 in urine.....	0·0098

Comparing with them the urine of 24 paralysed horses, no appreciable difference was found.

Coitus greatly increases the total quantity of urine and urea; the phosphoric acid is also increased, but not nearly so much in proportion. Only one experiment of this kind, however, was performed. W. D. H.

Obstructive Jaundice. By V. HARLEY (*Brit. Med. J.*, 1892, ii, 397—402).—The following are the main conclusions arrived at from experiments on dogs :—

1. In obstruction of the bile ducts the bile is absorbed from the liver by the lymphatics, not by the blood vessels. This occurs even after the ligature of the thoracic duct by supplementary ducts which soon form.

2. After ligature of the common bile duct, the pent up bile becomes concentrated, especially in so far as its less soluble constituents (cholesterol and mucin) are concerned.

3. The animals not only lived, but often gained in weight, after ligature of the common bile ducts. Therefore the admission of bile into the duodenum is not essential to life.

4. Ligaturing the thoracic duct not only prevents the occurrence of obstructive jaundice after the occlusion of the common bile duct, but checks it even after it has set in. W. D. H.

Transformation of the Albumin of the Urine in Bright's Disease. By E. GÉRARD (*J. Pharm.* [5], **26**, 104—106).—The urine of a patient passed during 24 hours contained 10—16 grams of albumin when the milk treatment was commenced. Two days later, the urine contained no albumin coagulable by heat alone; but nitric acid gave an abundant precipitate, soluble in excess of the reagent. A saturated sodium chloride solution caused an abundant flocculent precipitate, which the addition of acetic acid still further increased. These

various reactions are characteristic of propeptones. Further, it was possible to discriminate between the different compounds which according to Kühne make up the propeptones thus:—Heteroalbumose and protalbumose, precipitable by sodium chloride, and deuteroalbumose, only precipitable by excess of ammonium sulphate. To determine the amount of propeptone contained in this urine, acetic acid is added, and an excess of sodium chloride; about 24 hours afterwards there is added to the solution one-tenth its weight of ammonium sulphate. The precipitate is washed with water containing a little sodium chloride and ammonium sulphate. The propeptones thus separated are redissolved in water acidified by acetic acid, precipitated by absolute alcohol, dried, and weighed. At the beginning of the milk treatment, about 6·5—7 grams of propeptones was secreted in 24 hours, later this diminished to 1·9—2·6 grams. After some time, the patient was fed with yolk of egg, then ordinary food. The urine never contained albumin coagulable by heat, but always propeptones. Hence under the milk treatment, the albumin of urine in Bright's disease can be replaced by albumin partially digested. Further it is not sufficient to seek only for albumin coagulable by heat; it is equally necessary to examine for other albuminous principles, and amongst others the propeptones which are formed under the lactic treatment, and whose presence indicates phases of the pathologic state. J. T.

Phloridzin Diabetes. By M. Cremer and A. Ritter (*Zeit. Biol.*, 27, 459—465).—Experiments on hens and rabbits are recorded, which show that diabetes may be induced, not only by feeding animals on phloridzin or phloretin, but also by subcutaneous injection of these substances. The sugar appears to originate chiefly from proteïd metabolism. The close interdependence of this subject with glycogen formation is pointed out, and the rabbit is recommended as a suitable animal for working out this question more fully. W. D. H.

Pancreatic Diabetes. By V. Harley (*Brit. Med. J.*, 1892, ii, 451—454).—The view advanced by Lépine that the sugar in the urine of patients suffering from pancreatic diabetes is due to the absence of a glycolytic pancreatic ferment in the circulation is accepted. Certain toxic symptoms (tissue waste and muscular weakness) are considered to arise from the retention in the organism of certain excrementitious substances (leucomaïnes). W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Difference between Formed and Unformed Ferments. By M. Arthus and A. Huber (*Arch. de Physiol.*, 1892, 651—663).—Sodium fluoride, to the amount of 1 per cent. of the solution, kills all living things, and thus stops fermentations caused by micro-organisms. It does not stop fermentations caused by enzymes. W. D. H.

Influence of Antiseptics on Fermentation. By E. Biernacki (*Pflüger's Archiv*, **49**, 112—140).—All antiseptic agents have the property, under certain conditions, especially in small doses, of increasing alcoholic fermentations. The more powerful the antiseptic properties, the more powerful also is this action. The increase in alcoholic fermentation, and the same is true for fermentative and putrefactive processes generally, occurs with larger doses if very large quantities of the fermentable substances are present also. Organic substances appear to have the power in question to a greater degree than those of inorganic nature, and the richer an organic compound is in carbon, the more powerful it is. Among benzene derivatives, the greater the number of hydroxyl atoms, the weaker is the antiseptic, both as regards its antisepticity and its power in small doses of accelerating the fermentation. A mixture of antiseptics increases antifermentative action. The combination of organic with inorganic compounds is more powerful than a mixture of organic substances. W. D. H.

The Power of Propagation of the Leguminous Bacteria in Soil. By F. Nobbe, E. Schmid, L. Hiltner, and E. Hotter (*Landw. Versuchs-Stat.*, **41**, 137—138).—It was repeatedly observed that root nodules produced by inoculation from above only developed on the upper portions of the roots. This may be due to a want of sufficient oxygen in the subsoil, or to the inability of the organisms to reach the subsoil. To clear up this point, five peas were planted on 16th May, in non-nitrogenous and sterilised soil (with minerals); and on 26th June, after nitrogen hunger had commenced, were inoculated with an emulsion of pure cultures of pea-nodule bacteria (5 c.c. for each plant) at a depth of 200 mm. By the 20th July, the plants no longer showed nitrogen hunger, and on the 31st four of the dark-green plants (1150 mm. high) had 14—16 leaves, 1—2 pods, and 2—4 flowers. The fifth plant was somewhat behind the others. When taken up (2nd October) nodules were found only on the lower roots (both on roots of the second and first order) where inoculated. The upper parts of the roots were quite free from nodules. In a second experiment, in which the infecting material was introduced into the centre of the pot about 120 mm. deep, the result was similar, the nodules forming on the corresponding portion of the root. A similar result was obtained by infecting the upper and lower portions: the intermediate parts of the root remained free from nodules.

The nodules are generally situated on roots of the first and second order; in the case of late infection, on roots of the third order. It is the young roots which are capable of being infected, so long as they have susceptible hairs. This explains why late infection at the surface is often without effect. The age of the plant, provided that the roots are normal, has nothing to do with nodule formation. There seems to be no rule as to the position of the nodules, apart from the presence of the nodule organisms. N. H. M.

Assimilation of Formaldehyde by Green Plant Cells. By T. Bokorny (*Chem. Centr.*, 1892, ii, 80; from *Landw. Jahrb.*, **21**, 445—465). —It is shown that plants which have been deprived of starch, and placed in an atmosphere freed from carbonic anhydride, are capable

of forming considerable quantities of starch if fed with the sodium hydrogen sulphite compound of formaldehyde, and placed in a strong light. In the dark, no conversion of formaldehyde into starch takes place. C. F. B.

Carotene. By O. Hesse (*Annalen*, **271**, 229—230).—In the author's opinion the colorimetric method employed for the detection of carotene in plants is not a satisfactory one, inasmuch as other coloured compounds of like behaviour, such as rubidin, doubtless occur in the green parts of plants. F. S. K.

The Physiological Meaning of the Root Nodules of Eleagnus angustifolius. By F. Nobbe, E. Schmid, L. Hiltner, and E. Hotter (*Landw. Versuchs-Stat.*, **41**, 138—140).—Various experiments were commenced in 1891 to ascertain the physiological meaning of the root nodules of various non-leguminous plants (*Eleagnus*, *Hippophæ*, and *Alnus*). *Eleagnus* sprouts were planted in two pots containing sterilised nitrogen-free sand; the one pot, a week afterwards, was infected with an extract of *Eleagnus* soil. The infection had no visible effect during the whole summer, but in the autumn, one of the plants began to acquire a somewhat fresher green colour than the others, and in the spring of the following year this plant was unmistakably more vigorous than the others; it was strong and had side shoots. All the plants (of both pots) were isolated in nitrogen-free sand, when it was seen that only the plant which was benefited by the inoculation had nodules. On the 5th of September the main stem of this plant was 530 mm. high with 54 leaves and three side shoots 350, 325, and 105 mm. long. The non-infected plants and those which were unsuccessfully infected had an average height of 140 mm., were scanty and without side shoots. Only one of the infected plants began to get greener in July, 1892; it had three small oblong nodules when taken up.

There is no doubt that *Eleagnus* is enabled by the possession of nodules to utilise free atmospheric nitrogen. The organisms which produce these nodules were obtained in pure cultivations and are totally different from *Bacterium radicicola*. N. H. M.

The Nitrogen Question. By A. Petermann (*Mém. Acad. roy. Belg.*, **47**, 1892; compare Abstr., 1890, 816).—The first series of experiments now described were made with haricots and barley; each experiment consisted of four pots each with three haricot or six barley plants, the produce and sand of the four being mixed at the end of the experiments. The pots were kept in a glass-house and watered with well-water, which was analysed from time to time. In each case there were two experiments with sand alone, microbe-seeded with soil extract (1 and 1'); and two with sand, mineral manure, and microbe-seeded (2 and 2'). Each pot contained 4·5 kilos. of sand (containing 0·000633 nitrogen per cent.), that is, 18 kilos. for each experiment.

The haricots grew well and flowered, but those in the pots to which minerals were applied were stronger and greener than the others. The barley of the mineral pots grew well and produced ears; those

grown without minerals remained small and soon became yellow. The roots of the haricots had nodules, but they were much smaller than the lupin nodules.

The following amounts of dry matter (tops and roots) were produced in each experiment of four pots:—

	1.	1′.	2.	2′.
Haricots	15·70	16·68	28·06	29·8
Barley	15·50	16·93	57·14	45·42

The nitrogen was determined in the soil, seeds, and water as used, and in the soil and produce at the end of the experiments. The results are given in the table on p. 35.

An experiment was made simultaneously with those just described in which two more pots, each with 4·5 kilos. of sand, were exposed to air, being kept moist the whole time. The nitrogen of the sand and water amounted, in each case, to 0·0333 gram; at the end of 103 days 0·0247 and 0·0283 gram was found, being a loss of 0·0086 and 0·0050 gram of nitrogen respectively.

The experiments confirm the earlier ones (*loc. cit.*) in which lupins were shown to acquire nitrogen from the air. They also show a gain of nitrogen from the air in the case of barley, which is non-leguminous and has no nodules. The author concludes, therefore, with Frank,* that root nodules are not a general cause of nitrogen fixation, but assist in special cases.

The second series of experiments was made to ascertain whether the gain of nitrogen was due to the free or the combined nitrogen of the air. For these experiments, the tanks, or pits, employed in the earlier ones (*loc. cit.*) were used, but were now covered with a glass case 7·2 m. long, 1·2 m. wide, and of an average height of 1·1 m. This was divided into six compartments, one for each pit, each carefully isolated. There was also an arrangement for watering, and an aspirator, by means of which air could be made to pass through the cases. Nos. 1, 2, and 3 had ordinary air, Nos. 4, 5, and 6, air freed from nitrogen compounds. The pits contained each 1 cub. m. of sand weighing 1435 kilos. and containing 0·000228 per cent. of nitrogen and the necessary minerals; 250 c.c. of soil extract was also given. The following seeds were sown:—pits 1 and 6, 26 haricots; pits 2 and 4, 72 barley; pit 3, 45 lupins and pit 4, 36 lupins.

The plants developed well; the haricots and lupins flowered and produced seed, and the barley grew to the height of the cases. When the plants were taken up, the surface of the sand was found to be partially covered with chlorophyllous algæ. The roots of the haricots

* In a criticism of Frank's paper "On the Assimilation of Free Nitrogen," &c. (Abstr., 1892, 270), Kreusler points out (*Bied. Centr.*, **21**, 257) that Frank's method of analysis was not sufficiently exact to justify this conclusion (that non-leguminous plants fix free nitrogen), or any other. Thus, the small differences in the percentages of nitrogen in the soil at the beginning and end of the experiments, when calculated on the amounts of soil analysed (7—9 grams), become extremely small, quite within the unavoidable error of experiment. On the other hand, this small gain, when calculated on the total soil employed, becomes very great, far greater than the gain of nitrogen in the produce. There is, therefore, no reason why the plant nitrogen should not be assumed to have been derived from the soil.—N. H. M.

TABLE I.—*First Series*

	Nitrogen (in grams).							
	At commencement.	At conclusion.						
	In soil,* seeds, and water.	In soil.				In produce.	Total.	Gain.
		Organic.	As ammonia.	Nitric.	Total.			
				Haricots.				
1.....	0·2438	0·0671	0·0156	0·0234	0·1061	0·4141	0·5202	0·2764
1′.....	0·2438	0·0611	0·0156	0·0156	0·0923	0·4000	0·4923	0·2485
2.....	0·2462	0·0691	0·0091	0·0221	0·1003	0·4904	0·5907	0·3445
2′.....	0·2462	0·0611	0·0120	0·0192	0·0923	0·4672	0·5595	0·3133
				Barley.				
1.....	0·1950	0·0691	0·0156	0·0338	0·1185	0·3288	0·4473	0·2523
1′.....	0·1950	0·0550	0·0234	0·0052	0·0836	0·3027	0·3863	0·1913
2.....	0·2344	0·0601	0·0117	0·0169	0·0887	0·4973	0·5860	0·3516
2′.....	0·2344	0·0550	0·0117	0·0169	0·0836	0·4218	0·5054	0·2710

* The nitrogen of the soil was 0·1140 gram in each case. The nitrogen in the seeds was: haricots, 0·0624; barley, 0·0120 gram.

TABLE II.—*Second Series.*

	Nitrogen (in grams).							
	At commencement.			At conclusion.				
	In soil* and water.	Seeds.	Total.	Soil.	Drainage.	Produce.	Total.	Gain.
				Haricots.				
1.....	3·4311	0·1869	3·6180	5·1115	0·0509	0·9017	6·0641	2·4461
6.....	3·4311	0·1869	3·6180	4·6681	0·0697	0·6979	5·4357	1·8177
				Lupins.				
3.....	3·5074	0·4060	3·9134	5·8562	0·0189	6·6898	12·5649	8·6315
4.....	3·5074	0·3247	3·8321	5·5248	0·0158	8·0756	13·6162	9·7841
				Barley.				
2.....	3·4494	0·0364	3·4858	6·0227	0·0389	1·0416	7·1032	3·6174
5.....	3·4494	0·0364	3·4858	5·7443	0·0555	1·0572	6·8570	3·3712

* The amount of nitrogen in the soil was in each case 3·2756 grams.

had nodules from the size of a pin's head to that of hemp seed; the lupin nodules were sometimes as large as a hazel nut.

The following table shows the amount of dry produce (in grams) from each of the three pits, (1) with ordinary air, (2) with air freed from combined nitrogen :—

	Haricots.	Lupins.	Barley.
1. (Pits 1, 3, and 2).....	29·06	267·72	94·38
2. (Pits 6, 5, and 4).....	23·15	352·64	94·03

The nitrogen results are given on p. 36.

The nodules (dried) of the two lupin pits weighed, respectively, 6·37 and 8·00 grams, and contain 4·591 and 4·490 per cent. of nitrogen.

The whole of the results taken together prove the intervention of atmospheric nitrogen, not only in the case of lupins and haricots, but also in that of barley, and in those of the second series, prove further that the gain depends essentially on the fixation of elementary nitrogen. At the same time, the intervention of combined nitrogen is manifest in the results obtained with haricots and barley.

In conclusion, the author considers that if the difference of his results from those of Boussingault and all his successors who employed ignited soil gives rise to the idea of ascribing the utilisation of free nitrogen to intervention of soil micro-organisms, even in the case of the Gramineæ, it must be recognised that it is by no means proved that reactions of another kind do not take place, as, for instance, the direct assimilation of nitrogen by vegetable cellulose, which was certainly insufficiently demonstrated by Ville, but which received strong support from Frank's results (see footnote, p. 34). To clear up this point, it will be necessary to grow barley in sterilised, and in infected soil in an atmosphere free from combined nitrogen.

N. H. M.

Chemical Composition of Apples and Pears, especially with regard to their Utilisation for Fruit Wine. By P. Kulisch (*Bied. Centr.*, **21**, 700—702; from *Landw. Jahrb.*, 1892, 427).—The examination of a large number of varieties of apples showed that the amount of cane sugar varies both absolutely and in relation to the amount of invert sugar. When the apples are detached from the tree, cane sugar continues to be produced from the starch present, but, finally, the cane sugar becomes almost completely converted into directly reducing sugar. There is no relation between the amount of cane sugar and acid, and a high percentage of acid does not result in a lower percentage of sugar. The suitability of a particular kind of fruit for wine depends on other properties besides the amounts of determinable constituents, the knowledge of which is chiefly of use in mixing the various kinds of most. Addition of water or sugar with a view to improving most is to be avoided. 5·5—6 per cent. of alcohol is sufficient for fruit wine.

There seems to be no relation between the fertility of the trees and the percentage of sugar in the fruit, although the number of apples has great influence on the weight of the single apples. Large apples

* The amount of nitrogen in the soil was in each case 3·2756 grams.

contain, however, a greater percentage of sugar than small apples from the same tree.

With regard to the presence of cane sugar in pears, the author found, contrary to his early results, sugar in those which had been kept to ripen; this requires further investigation.

Currants, gooseberries, blackberries, and mulberries contain only traces of cane sugar, whilst most stone fruits contain much. No considerable amount of cane sugar could be found in raspberries and bilberries. N. H. M.

Chemistry of the Tobacco Plant. By R. J. DAVIDSON (*Exper. Stat. Record*, **4**, 30—31; from *Virg. Stat. Bul.*, No. 14, 1892).—The following table shows the average percentage amounts of dry matter, nitrogen, and ash-constituents in the air dried leaves, stems, and roots of four varieties of tobacco:—

	Dry matter.	Nitrogen.	P_2O_5.	K_2O.	CaO.	MgO.	Insoluble matter.
Leaf.....	92·38	4·37	0·502	5·738	5·449	0·956	1·943
Stem	93·82	3·71	0·646	5·020	2·222	0·593	0·662
Root	93·75	1·88	0·211	1·777	1·277	0·208	2·877

With regard to the relative amounts of leaf, stem, and root, the averages for all four varieties are respectively 55, 21·9, and 23·1 per cent. A crop yielding 1000 lbs. of leaves would contain an average amount of 66·85 lbs. of nitrogen, 8·68 lbs. of phosphoric acid and 85·41 lbs. of potash distributed as follows:—

	N.	P_2O_5.	K_2O.
In leaves.....	43·7 lbs.	5·0 lbs.	57·4 lbs.
In stems.....	15·2 „	2·7 „	20·5 „
In roots	7·9 „	1·0	7·5 „

About one third of the fertilising constituents are, therefore, in the roots and stems, which should be returned to the soil.

N. H. M.

Manufacture and Composition of Linseed Cake and Meal. By HASELHOFF (*Landw. Versuchs-Stat.*, **41**, 55—72).—Flax is chiefly grown in Germany for the flax; for seed it is almost only grown in Mecklenburg and Königsberg, and the seed is not of very good quality for the production of oil. The American seed is of about the same quality; the Indian (Bombay) is better, whilst the best seed is that from Russia, especially South Russia. Most of the impurities are removed by sifting; when there remains only 4 per cent. of foreign matter (or even 8 per cent. if the foreign matter consists of oily seeds), the seed is practically pure. With regard to the manufacture of linseed oil, the original method consisted in pounding the seeds. Now there are two methods by which the oil is pressed out; in the one heat is applied to the vessel containing the seeds (either by direct firing or

steam), in the other the seed is directly treated with superheated steam. Another method is to extract with light petroleum. The residue (cake or meal) varies in composition according to the method employed. Thus, whilst the residue from pressed seeds contains about 32—36·4 per cent. of proteïn and 9—11 per cent. of fat, the residue from extracted seeds contains more proteïds (40 per cent.) and less fat (3—4 per cent.). The amount of mucilage also varies; where direct steaming is employed the amount is diminished, and cake so obtained will keep for years without becoming mouldy. This is also the case with cake prepared by the light petroleum method, but this seems to be due, not to the abstraction of mucilage, but to the action of the light petroleum.

For adulteration, not only vegetable substances but also heavy spar, gypsum, chalk, and salt are employed; saw-dust has been found. Rape-cake meal may be detected by stirring in water in a glass cylinder and allowing to settle; if any dark particles are visible, rape is probably present. A few drops of aqueous alkali will give an intense yellow colour if rape is present. Amygdalin does not seem to be actually injurious, but mustard, corn-cockle, and *Camelina* are said to be injurious, whilst castor oil is poisonous and may cause death. Vegetable impurities can mostly only be detected microscopically and the amounts only approximately estimated. But the amount of fat, and especially of proteïn, give a good idea as to purity or otherwise. When mineral impurities are present they may be detected by the amount of ash, which generally should not exceed 5 per cent. Cake containing over 14 per cent. of water cannot be considered as pure.

With regard to fat, it should be noted what results are obtained when the substance is (1) not previously dried, (2) when dried for two hours at 100—105°, and (3) when dried for two hours at 100° in an atmospbere free from oxygen; the results should not differ. The rancidity of the fat is determined (1) after the fat has been so long dried that it no longer has an unpleasant odour, and (2) without previous drying. The first estimation gives a lower result than the second, from loss of volatile fatty acids. The higher the percentage of acid the greater the difference in the two experiments; the estimation of rancidity of linseed residues and in foods generally should therefore be made in the fat from undried substance. The cake and meal were also examined bacteriologically; large numbers of micro-organisms were found, but the results give no indication of the quality of the substance examined, as the nature (injurious or otherwise) of the micro-organisms is not known. N. H. M.

Manufacture and Impurities of Linseed Cake. By F. J. VAN PESCH (*Land. Versuchs-Stat.*, **41**, 73—93).—Only very little of the linseed worked in Holland is produced in that country; much is obtained from Russia, but most from India. The composition of samples of cake examined at Wageningen varied as follows: proteïds (22—37), fatty matter (6·2—18·5), starchy matter (30), water (11—16), ash (4·5—8·6), and crude fibre (7·3—12·3 per cent.). The average amount of digestible matter (according to Kühn) would

therefore be:—proteïds 26, fatty matter 10·4, and starchy matter 24·3 per cent. The origin of the seed has a great influence on the quality of the cake. According to Voelcker, the Russian seeds contain most albumin; those grown further south contain the most fat. The method for the microscopic examination of linseed was described by Kobus, (*Landw. Jahrb.*, 1884, 120). The chief weeds which occur in linseed are *Polygonum convolvulus* and *lapathifolium*; rape is very frequent, whilst *Camelina dentata*, *Galium aparine*, *Thlaspi arvense*, and *Agrostemma githago* also occur. Less frequent are *Brassica nigra*, *Sinapis arvensis*, *Plantago lanceolata*, *Lolium*, and other grasses. Besides these seeds which occur naturally, stalks and sand are sometimes found. In Belgium rice meal and earth-nut skins are frequently added.

Cake manufactured by the so-called American method, in which the finely-powdered seed is extracted by carbon bisulphide, only contains 3—4 per cent. of fatty matter, and is therefore not used in Holland. The method employed for the examination of cake is as follows. The sample is made to pass through a 5 mm. sieve, and 5 grams stirred in a beaker with 100 c.c. of boiling water. Beakers of one size are employed, so that the more or less swelling of the powdered cake and the smaller or greater amount of liquid which separates can be compared. It is also noticed whether the liquid is quite thin or whether it is slimy. With regard to the swelling up, *Camelina* swells considerably more than linseed. Kobus (*loc. cit.*) found that 1 gram of linseed kept in water for one hour weighed 2·7—2·8 grams, whilst 1 gram of *Camelina* weighed 4·4 grams after the same treatment. A part of the liquid is tested with iodine for starch; only a light blue colour should be produced. The residue obtained when the water is poured off is examined microscopically (Kobus, *loc. cit.*). The number of foreign particles is estimated in 5 grams, the separation being effected by a jet of water on the substance in a 1·2 mm. sieve. Determinations of proteïds, fat, and ash are also made.

The injurious substances sometimes found in linseed cake are corncockle, containing a poisonous substance, saponin or githagin, the seeds of *Thlaspi arvense*, which, when eaten by cows, impart a garlic-like taste to the milk, and hemp seed, which causes diarrhœa. Barium sulphate is objectionable, whilst salt, besides being good for cattle, has the advantage of making the cake softer; on the other hand, the cake becomes quickly moist and therefore spoilt. The poisonous action of castor oil beans was first shown by van den Berghe. Other substances doubtless occur which are more or less poisonous or injurious when much of them is present.

The results of experiments made at Wageningen show that in 5 grams of substance it requires only 16 seeds of *Polygonum lapathifolium*, 13 of *P. convol.*, 4 of *Galium aparine*, and 46 of *Camelina* to make 1 per cent. of the cake. Each seed is reckoned as follows:—*Camelina* 2, *Polygonum lap.* 6, *P. convol.* 8, *Galium aparine* 25; if the sum of the numbers found exceeds 100, the cake is not pure enough.

In most cases it is sufficient to magnify 70—80 times, but in some cases 300 times. For the detection of very finely-powdered substances in cake, a test tube is half filled with the powdered cake, treated with

alcohol, well shaken, and allowed to settle; the alcohol is poured off and some of the fine meal which floats on it put on an object glass. The alcohol is evaporated, a drop of glycerol and aqueous soda added and pressed with a second glass. When magnified 300 times, earth-nut meal is readily distinguished; it is seen as ring-shaped depressions. Other substances than earth-nut meal can only be detected by special methods. N. H. M.

Analytical Chemistry.

Improvements in Gasvolumeters. By G. LUNGE (*Ber.*, **25**, 3157—3164).—Arrangements are here described for closing the "reduction tube" of the gasvolumeter (Abstr., 1890, 660) other than by the use of a stop-cock or by sealing the end, both of which methods have certain disadvantages. By suitably adjusting the levels of the mercury in the "reduction" and "measuring" tubes, it is possible to employ the instrument for the measurement of both moist and dry gases, as also to use it as a "gravivolumeter" (compare Japp, Trans., 1891, 894; Lunge, Proc., 1891, 170). A. R. L.

Titration Apparatus with Automatic Zero Adjustment. By S. KRAWCZYNSKI (*Ber.*, **25**, 3010—3011).—Into one neck of a two-necked Woulff's bottle of suitable capacity is fixed by means of a cork, a burette consisting of an inner and outer tube; and to the other neck of the bottle is fastened a small, two-bladder hand bellows and a side tube for releasing the air pressure after the burette is filled. The inner tube of the burette is open at both ends, reaches nearly to the bottom of the Woulff's bottle, and ends about 5 cm. below the top of the outer tube, this point being the zero mark. The outer tube, fused on to the inner tube just above the cork, is graduated, and has an ordinary burette tap fused into the side near the bottom. E. C. R.

Estimation of Free Acids in the presence of Acid Phosphates. By J. WAGNER (*Pflüger's Archiv*, **50**, 375—384).—Leo's method (Abstr., 1891, 1288) is again criticised and declared to be wholly worthless. W. D. H.

Estimation of Chlorine in Electrolysed Solutions. By L. M. NORTON (*Chem. News*, **66**, 115—116).—For the estimation of total chlorine and chlorine as chloride, hypochlorite, and chlorate in electrolysed or other solutions, the author mentions various methods, but regards the following mode of procedure as most convenient. The chlorine present as hypochlorite is estimated by titration with sodium arsenite in the usual manner, then by titrating an aliquot part of the same solution with silver nitrate, and deducting the chlorine present as hypochlorite from the result, the amount of chlorine present as chloride is found. The total chlorine is estimated in a fresh portion by treat-

ing it with saturated aqueous sulphurous acid to reduce chlorate, and employing Volhard's method of adding excess of standardised silver nitrate, and titrating back with ammonium thiocyanate in the presence of ferric alum. The difference between this result and the sum of the chlorine present as chloride and hypochlorite gives the amount present as chlorate. D. A. L.

Estimation of Bromine and Iodine in presence of Chlorine. By E. Nihoul (*Zeit. angw. Chem.*, 1891, 441).—The author has attempted to substitute hydrogen chloride for chlorine in the well known indirect process of determining the amount of the three halogens when precipitated as silver salts. Silver bromide is completely converted into chloride when heated for an hour in a current of hydrogen chloride, but unfortunately silver iodide is but partially decomposed, and as the action of chlorine is complete in about 10 minutes, the author is not inclined to give up the use of that gas. L. de K.

Estimation of Nitrogen in Nitrates. By Alberti and Hempel (*Zeit. angw. Chem.*, 1891, 398—400).—Fricke (compare Abstr., 1892, 527) strongly recommended Ulsch's process for the estimation of nitrogen in nitrates. The authors have also investigated the method, and as the results of numerous experiments, now propose its universal introduction in agricultural chemical stations. Their test analyses, practised not only on pure and commercial nitrates, but also on complex manures, are very satisfactory. L. de K.

Estimation of Nitrogen in Nitrates. By K. Ulsch (*Zeit. angw. Chem.*, 1891, 719).—The success of the author's process depends, of course, greatly on the accurate estimation of the ammonia obtained by reducing the nitrate by means of sulphuric acid and metallic iron. The author now puts into the receiver a quantity of N/5 acid slightly insufficient to neutralise all the ammonia which is given off on distilling the liquid with excess of sodium hydroxide. More acid is then carefully added until exact neutrality is obtained. The results thus obtained are more trustworthy than those got by the usual procedure of using excess of acid, and then titrating back with alkali. L. de K.

Iodometric Estimation of Nitrates. By F. A. Gooch and H. W. Gruener (*Amer. J. Sci.*, **44**, 117—123).—The authors recommend distilling the nitrate (about 0·2 gram) with 20 c.c. of a saturated solution of crystallised manganous chloride in strong, hydrochloric acid, in a current of carbonic anhydride. The products of the distillation are passed into a solution of potassium iodide, and the liberated iodine is afterwards titrated by means of sodium thiosulphate. 3 mols. of iodine correspond with 2 mols. of hydrogen nitrate.

The apparatus employed consists of a bent pipette, serving instead of a retort, which is connected with a Kipp's apparatus evolving carbonic anhydride. The other goose-neck like end is sealed to a Will and Varrentrap nitrogen bulb, the exit tube of which is drawn out, so that it may be pushed well within the inlet tube of a Will and

Varrentrap absorption flask. A third receiver simply acts as a trap to exclude air from the absorption apparatus proper. The titration should be completed immediately after the distillation, during which the nitrogen bulbs should be immersed in cold water; otherwise, traces of dissolved nitric oxide might get oxidised and liberate more iodine. The test analyses are very satisfactory. L. DE K.

Estimation of Nitrous Acid in Sodium Nitrate. By O. REITMAIR and A. STUTZER (*Zeit. angw. Chem.*, 1891, 666—667).—The authors have come to the conclusion that the estimation with potassium permanganate gives erroneous results, and that for accurate determinations, Lunge's process should be adopted (compare Abstr., 1892, 1029). L. DE K.

Determination of Nitrogen in Soils by Kjeldahl's Method. By J. A. MULLER (*Ann. Chim. Phys.* [6], **22**, 393—401.—A number of comparative determinations have shown that when the nitrogen in soils is estimated by Kjeldahl's method, the results come out, as a rule, a little lower than when the soda-lime process is employed; the difference is, on the average, 0·04 gram of nitrogen per kilo. of dry soil. It is necessary, however, to add a little benzoic acid to the mixture of soil and fuming sulphuric acid; otherwise the results may fall out much too low.

The apparatus employed by the author consisted of a small, long-necked flask, of about 75 c.c. capacity, heated in an air-bath; the neck of the flask, projecting from the air-bath, was bent downwards and introduced into a small flask, so that any sulphuric acid which was volatilised during the process would not run back down the sides of the hot vessel and cause fracture.

The proportions taken were:—15 grams of the dry, finely-divided soil, 30 c.c. of fuming sulphuric acid, and about 0·3 gram of benzoic acid. The operation occupies about 12 to 18 hours, during which time the temperature is gradually raised; towards the end of the operation, the mixture is heated sufficiently to distil about 1·5 c.c. of the sulphuric acid.

The soils examined were free from, or contained only traces of, nitrates. F. S. K.

Estimation of Phosphorus in Steel. By H. WDOWISZEWSKI (*Chem. Centr.*, 1892, ii, 56—57; from *Stahl u. Eisen*, **12**, 381).—The following combination of hitherto known methods is proposed; it is asserted that an accurate estimation can be made in two hours. 2—5 grams of steel is dissolved in 30—75 c.c. of nitric acid (sp. gr. 1·2) in a conical flask of 300—500 c.c. capacity, the boiling solution is treated with 10—25 c.c. of a 1 per cent. permanganate solution, and boiled until the precipitated manganese dioxide rapidly sinks to the bottom, when the flask is removed from the flame. 2 c.c. of concentrated hydrochloric acid is now added for every gram of steel taken, and the boiling is continued until the dioxide has completely dissolved, and all the chlorine is driven off. The solution is then treated with strong ammonia in considerable excess, being shaken

continually the while, and to the gelatinous mass strong nitric acid is added little by little in quantity more than sufficient to dissolve the precipitate. The solution is then heated to 85°, 25—30 c.c. of ammonium molybdate is added, and the flask is stoppered and shaken gently, the stopper being removed occasionally, and, finally, wrapped in a cloth and shaken violently for five minutes. The precipitate is collected with the aid of the pump, washed with 15 per cent. ammonium nitrate, and then 2—3 times with water, brought, together with the filter, into a flask, and treated with 6—10 c.c. of an ammonia solution standardised against phosphorus. After the precipitate has dissolved, the excess of ammonia is determined by titration with an equivalent solution of hydrochloric acid. The burettes used were graduated in 1/30 c.c.; 1 c.c. of the ammonia solution = 0·03534 per cent. of phosphorus. C. F. B.

Estimation of Phosphorus in Steel and Cast Iron. By R. Zimmermann (*Chem. Centr.*, 1892, ii, 131—132; from *Stahl u. Eisen*, **12**, 524—527).—A modification of Metz' method, occupying 30—35 minutes for steel, and two hours for cast iron, as in the latter case silica and graphite have to be separated. 5·0008 grams of the metal is dissolved in a tall beaker in nitric acid (sp. gr. 1·20), oxidised with permanganate, the manganese dioxide reduced with hydrochloric or oxalic acid, the clear solution treated with ammonium nitrate, and the phosphorus precipitated by a large excess of molybdate solution. After shaking for a few minutes, the beaker is inclined, the precipitate allowed to settle, and, after 15—20 minutes, the clear solution siphoned off. The precipitate is washed on a filter of 6—7 cm. diameter with dilute nitric acid of sp. gr. 1·002, then washed with this solution through a small funnel into a specific gravity bottle, which is filled and weighed (G = bottle + precipitate + solution). g (= bottle + solution) is then read off from a table, and $\frac{1}{2}(G - g)$ gives the percentage of phosphorus. C. F. B.

Rapid Estimation of Phosphorus in Iron, Steel, and Ores. By J. O. Handy (*Chem. Centr.*, 1892, ii, 185; from *J. anal. Chem.*, **6**, 204—211).—The method is based on the fact that precipitated ammonium phosphomolybdate, when freed from acid by washing with a neutral solution of potassium nitrate, is dissolved by standard soda, the excess of which may be determined by titration with nitric acid, phenolphthaleïn being used as an indicator. 2 grams of steel is dissolved in 75 c.c. of nitric acid (sp. gr. 1·13) in a conical flask, 15 c.c. of 0·5 per cent. permanganate solution added to the boiling solution, the whole boiled, about 0·03 gram of cane sugar added, and heated until the manganese peroxide has dissolved. The flask is then removed from the flame, 13 c.c. of ammonia (sp. gr. 0·90) is added, the whole is shaken, cooled to 85°, treated with 50 c.c. of molybdate solution, shaken for five minutes, and the precipitate collected, washed with 0·1 per cent. nitric acid, and then five times with 0·1 per cent. potassium nitrate solution. The filter and precipitate are then put back into the flask, 20 c.c. of standard soda, water,

and phenolphthaleïn are added, and the excess of soda titrated with nitric acid.

The molybdate solution is prepared by dissolving 1 lb. of molybdic acid in 1200 c.c. of water and 700 c.c. of ammonia (sp. gr. 0·9), adding 300 c.c. nitric acid (sp. gr. 1·42), and pouring the mixture, a quarter at a time, into four flasks each containing a mixture of 500 c.c. of nitric acid (sp. gr. 1·42) and 1200 c.c. water; no molybdic acid is precipitated. The soda and nitric acid solutions are standardised with pure, yellow ammonium phosphomolybdate containing 1·63 per cent. phosphorus. 0·014 per cent. of arsenic in the iron does not affect the determination of the phosphorus. C. F. B.

Precipitation of Phosphates and Arsenates by Ammonium Molybdate. By B. Moreau (*J. Pharm.* [5], **26**, 157—163).—The reagent is prepared by dissolving 12 grams of ammonium molybdate in 10—15 grams of warm water; to this is added a mixture of 145 grams of nitric acid and 30 grams of water. The solution is heated on the water-bath from 10 to 15 minutes, made up to a litre, and decanted after settling for some hours. In testing for phosphate or arsenate, 2 c.c. of the reagent is heated to boiling in a tube, taking care not to heat the surface, then some drops of the solution to be tested are added, boiled again if necessary, when a precipitate indicates a phosphate or an arsenate. 1 gram of phosphoric acid in 10 litres of water is faintly indicated, and 1 gram of arsenic acid in 1300 grams of water. Quantitatively, 60 c.c. of the reagent is heated nearly to boiling on the water-bath; it should remain clear, then 5 c.c. of nitric acid is added, 20 c.c. of the solution of phosphate or arsenate containing about 1 per cent., and, finally, 6—8 grams of ammonium nitrate crystals; it is then boiled for a quarter of an hour with frequent shaking. J. T.

Estimation of Carbon in Iron or Steel, also of Carbonic Acid in Aqueous Solutions. By G. Lunge and L. Marchlewski (*Zeit. angw. Chem.*, 1891, 412—414).—The authors (compare Abstr., 1892, 531) state that by using a larger flask and funnel, their apparatus is very suitable for the estimation of carbon in iron or steel. The following solutions are required:—1. A saturated solution of copper sulphate. 2. A solution of 100 grams of chromic acid in 100 c.c. of water. 3. A saturated solution of chromic acid in sulphuric acid of sp. gr. 1·65. 4. A similar solution in acid of sp. gr. 1·71. 5. Sulphuric acid of sp. gr. 1·1. 6. Commercial hydrogen peroxide. The process is carried out as follows:—0·5 gram of the sample (or a larger quantity if the sample is poor in carbon) is put into the flask and covered with 5 c.c. (or more in proportion) of the copper solution, which is allowed to act from 1 to 6 hours. Experiments made in the hope of accelerating the action by application of heat were unsuccessful. The mixture is now treated with the solution of chromic acid, 10 c.c. for every gram of the sample, then with the sulphuric acid of sp. gr. 1·65, of which 135 c.c. is used for 0·5 gram of sample, but only 130 c.c. for 1 or 2 grams. If more than 2 grams has been weighed out, from 75 to 70 c.c. of the sulphuric acid of sp. gr. 1·71 is used instead. Finally, sulphuric acid of sp. gr. 1·1 is

added; 30 c.c. for 0·5 gram of the sample, 25 c.c. for 1 gram, and 5 c.c. only for 2, 3, and 5 grams. Gentle heat is applied, when the carbon is rapidly oxidised to carbonic anhydride, which escapes into the measuring tube. To expel the last traces, from 1 to 2 c.c. of the hydrogen peroxide is introduced into the flask. This, when it comes in contact with the chromic acid, evolves oxygen, which sweeps out any carbonic anhydride. The mixed gases are measured as described in the previous paper, the carbonic anhydride is absorbed by aqueous soda, and so found by difference.

The test analyses are very satisfactory. It will be easily understood that the apparatus may be successfully employed for the estimation of free and combined carbonic acid in mineral waters.

L. DE K.

Estimation of Potassium as Perchlorate. By W. WENSE (*Zeit. angw. Chem.*, 1891, 691—693).—Owing to the high price of platinum chloride, other precipitants for potassium have been lately attracting attention, and more particularly perchloric acid. As, however, potassium perchlorate is decidedly soluble even in alcohol, its quantitative isolation is very difficult, but the author has vastly improved the method.

The commercial potash salts are freed from sulphates by the cautious addition of barium chloride, and the filtrate is then evaporated on the water-bath with a slight excess of perchloric acid until no more acid fumes escape. The residue is powdered and extracted with 96 per cent. (commercial absolute) alcohol, to which 2 per 1000 perchloric acid has been added, in which mixture the potassium perchlorate is all but insoluble. The insoluble mass is collected on a weighed filter (dried at 120°), and, finally, slightly washed with pure alcohol to remove the traces of free acid. After drying at 120°, the perchlorate may be weighed.

Perchloric acid may be conveniently prepared as follows:—1 part of potassium perchlorate is distilled in a strong retort with 2 parts of 90 per cent. sulphuric acid in a vacuum. The distillate is diluted, boiled, and freed from sulphate by cautious addition of barium chloride. After evaporating off any free hydrochloric acid, the liquid is again subjected to distillation. The author's test analyses are satisfactory.

L. DE K.

Estimation of Potassium. By F. JEAN and TRILLAT (*Bull. Soc. Chim.* [3], **7**, 228).—The platinochloride, having been precipitated and purified in the usual way, is dissolved in water, and the solution, made alkaline with soda, is warmed and reduced by the addition of a few drops of aqueous formaldehyde; it should be stirred with a glass rod to prevent the platinum adhering to the vessel. The metal is then collected in the usual way.

JN. W.

Separation of Magnesium Chloride from the Chlorides of Sodium and Potassium. By R. B. RIGGS (*Amer. J. Sci.*, **44**, 103—109).—Gooch (*Amer. Chem. J.*, **14**, 33) has shown that both potassium and sodium chlorides are insoluble in anhydrous amyl alcohol, and may in this way be separated from the soluble lithium chloride.

He also called attention to the solubility of anhydrous magnesium chloride. The author found, however, a great difficulty in dehydrating this chloride without decomposition, but succeeded at last by adding to the amyl alcohol a few drops of benzyl chloride. This addition is, however, unnecessary when the mixed chlorides are treated as follows:—They are dissolved in as little water as possible and a few drops of hydrochloric acid added. 30 to 40 c.c. of amyl alcohol is then added and the water boiled off; the boiling is continued until the volume of the liquid is reduced to about 10 c.c. In filtering it is of great advantage to use a perforated crucible and an asbestos felt, and to filter under pressure. In case the total chlorides exceed 0·2 gram, the residue must be redissolved in a few drops of acid, and once more boiled with amyl alcohol; the filtrate is transferred to a weighed platinum dish and evaporated. Water is added before all the alcohol has been expelled, and the evaporation continued. Finally a slight excess of sulphuric acid is added; the residue is gently ignited, and weighed as $MgSO_4$. L. DE K.

Detection of Strontium in presence of Calcium. By P. E. BROWNING (*Amer. J. Sci.*, **43**, 386—388).—The author (Abstr., 1892, 915) has shown that calcium may be quantitatively separated from strontium by dissolving the mixed nitrates in a few drops of water and boiling with amyl alcohol. When the process is applied qualitatively, it will be found that, even in the absence of strontium, a slight deposit will form on the bottom of the test tube in which the boiling takes place. If this precipitate, after being washed with amyl alcohol, is redissolved in a drop of dilute nitric acid and again boiled with the amyl alcohol, it separates out wholly or partially. The author thinks that the deposit consists of the calcium salt of an organic acid formed by the action of the nitric acid on the fusel oil.

If, however, the deposit is first gently ignited before dissolving it in the nitric acid, it will completely dissolve in the amyl alcohol, and with care very minute proportions of strontium may be detected in presence of calcium. L. DE K.

Estimation of Barium in the presence of Calcium and Magnesium. By F. W. MAR (*Amer. J. Sci.*, **43**, 521—525).—It is a well-known fact that barium chloride is practically insoluble in strong hydrochloric acid, but the author has found that in order to make this a quantitative means of separation, some ether should be mixed with the acid. To utilise the process for the separation of barium from calcium, or magnesium, about 1 gram of the mixed chlorides must be dissolved in the smallest possible quantity of boiling water and precipitated by 25 c.c. of fuming hydrochloric acid. After cooling, 5 c.c. of pure ether is added. The acid should be added very gradually, so as to get the barium chloride in a coarse crystalline condition, when it is less liable to include foreign matter. After standing a few minutes, the precipitate is filtered into a Gooch's crucible, washed with hydrochloric acid containing 10 per cent. of ether, dried at 150—200°, and weighed as $BaCl_2$.

The process, as shown by the test analyses, is accurate and rapid.

The fumes of the strong acid cause no inconvenience if the filtration is performed in front of a good flue. L. DE K.

Assay of Aluminium and some of its Alloys. By F. REGELSBERGER (*Zeit. angw. Chem.*, 1891, 442—446; 473—478).—*Estimation of Silicon in Aluminium*—The short process communicated by the author some time ago gives results which can never be scientifically correct, as some of the silicon escapes as hydride. Moreover, it does not distinguish between the two varieties of silicon. The new process is as follows:—4 grams of the cut up metal is dissolved, with the usual precautions, in a mixture of 30 c.c. of nitric acid, sp. gr. 1·35, and 70 c.c. of hydrochloric acid, sp. gr. 1·16. Whilst boiling, 30 c.c. of sulphuric acid is added and the evaporation continued until no more nitric fumes escape. About 200 c.c. of water is now carefully added and the insoluble matter is collected, washed and ignited in a platinum crucible. The product is crude silicic acid, which is weighed. It is then evaporated with hydrofluoric acid; the loss represents the silica. The residue is now again evaporated with hydrofluoric acid, but this time with the addition of nitric acid. The loss in weight represents the silicon. The red residue consists of a little ferric oxide.

Estimation of Aluminium in Ferro-aluminium.—5 grams of the alloy is dissolved in dilute sulphuric acid and heated until sulphuric fumes escape. The residue is then diluted with water to 300 c.c. 100 c.c. of the filtrate is reduced by boiling with iron wire or sodium hydrogen sulphite, then nearly neutralised with aqueous soda and poured into a boiling solution of 10 grams of potassium hydroxide in 50 c.c. of water mixed with 8 grams of potassium cyanide in 40 c.c. of water. The liquid is finally made up to 500 c.c. and 300 c.c. (= 1 gram metal) of the filtrate is boiled in a large porcelain dish with 15 grams of ammonium nitrate. The precipitate is thoroughly washed (best by means of a filter pump) and finally weighed as Al_2O_3. It may be further tested as to its absolute purity.

Assay of Aluminium-copper and Aluminium-zinc-copper. — (1.) *Estimation of silicon*—5 grams of the alloy is dissolved in nitro-hydrochloric acid, the solution evaporated to dryness, and the residue dissolved in dilute hydrochloric acid. Should the insoluble matter not be pure white, it must be fused with sodium potassium carbonate and the silica recovered from the melt as usual. The acid filtrate is added to the main filtrate. If the alloy is suspected to contain tin or lead, it is dissolved in nitric acid and evaporated with sulphuric acid. The insoluble matter is fused with the alkali carbonate, and then treated with nitric acid, when a mixture of silica and tin oxide will be obtained, in which the former may be estimated by evaporation with hydrofluoric acid. The lead will be found in the (nitric) acid filtrate. (2.) *Iron and aluminium*—If zinc is absent, an aliquot part of the filtrate is boiled with sodium thiosulphate to precipitate the copper as sulphide. The filtrate when poured into boiling potassium hydroxide yields a precipitate of ferrous oxide whilst the alumina dissolves, and may be recovered as usual. The iron precipitate may be obtained pure by redissolving it in nitro-hydrochloric acid and reprecipitating with ammonia. (3.) If zinc is

present, the mixed iron and aluminium is first precipitated by means of ammonium acetate. In the filtrate, the zinc may be very conveniently estimated volumetrically by the ferrocyanide process in the absence of manganese. (4.) The copper is best estimated by electrolysis. 3 to 5 grams of the sample is dissolved in nitric acid and evaporated, with addition of sulphuric acid, to a syrupy consistence. The mass is then dissolved in water, filtered, and made up to a definite bulk from which an aliquot part is taken for the electrolytic estimation. (5.) Manganese, if present, will be found in the iron precipitate (2), and may be recovered from it in the usual manner.

L. DE K.

Estimation of Aluminium in Steel, Bronze, &c. By W. SCHÖNEIS (*Chem. Centr.*, 1892, ii, 132; from *Stahl u. Eisen*, **12**, 527).—5—10 grams of steel turnings are dissolved in nitric acid (sp. gr. 1·2) in a large platinum dish, the solution evaporated to dryness, and the residue cautiously heated and finally ignited until all oxides of nitrogen are expelled. The residue is finely powdered in an agate mortar and fused in a silver dish with solid potash free from aluminium. The cooled mass is treated with hot water, filtered, and washed, and the aluminium in the filtrate precipitated by the addition of hydrochloric acid and ammonia. In the case of basic Martin steel, the alumina is pure; in the case of acid Martin steel, crucible steel, and ferro-aluminium, it contains silica, and must be treated with hydrofluoric acid.

C. F. B.

Separation of Iron, Aluminium, and Chromium. By C. MARCHAL and J. WIERNIK (*Zeit. angw. Chem.*, 1891, 511—513).—The two processes mostly used are the one introduced by Wöhler, who mixes the solution containing the three metals with potassium or sodium hydroxide in excess and then passes chlorine through the liquid until all the chromium has passed into the state of chromate, or the method proposed by Gibbs, who nearly neutralises the solution with sodium carbonate, adds excess of sodium acetate, and then oxidises by means of chlorine or bromine.

As, however, both processes fail, even qualitatively, if the amount of chromium is very small, the authors have searched for another oxidiser and found an excellent one in the shape of freshly precipitated manganese dioxide. To ensure success, the analysis must be carried out as follows:—The metals are, if possible, converted into sulphates or else into chlorides, and the solution is, as far as practicable, neutralised with sodium carbonate. Freshly-precipitated, well-washed manganese dioxide, prepared by mixing manganous sulphate (1 mol.) with potassium permanganate (1 mol.), is now gradually added, and the mixture boiled for about 10 minutes, which is generally sufficiently long to precipitate all the iron. The filtrate contains all the alumina and all the chromium as chromate, besides a little manganese, whilst the precipitate consists of ferric hydroxide and undissolved manganese dioxide.

To estimate the iron, the precipitate is dissolved in hydrochloric acid and boiled with sodium acetate. To free the iron precipitate completely from manganese, it must be redissolved in hydrochloric

acid and reprecipitated with ammonia. The filtrate is boiled and mixed with a little ammonia, which precipitates the alumina and also any manganese. The precipitate is then dissolved in hydrochloric acid, and treated with sodium acetate like the iron precipitate. The alkaline chromate is finally reduced as usual, and then precipitated with ammonia. The test analyses made on rather small quantities of a mixture of ferric, aluminium, and chromic oxides are fairly satisfactory. L. DE K.

Colorimetic Estimation of Iron. By J. RIBAN (*Bull. Soc. Chim.*, [3], **7**, 199—200; Abstr., 1892, 240, 1132).—The author maintains that Lapicque's thiocyanate method can only be carried out under very special conditions, owing partly to the dissociation of ferric thiocyanate in dilute solution, and partly to the impossibility of procuring standard coloured glasses of uniform colour. JN. W.

Estimation of Vanadium in Ores. By L. L'HÔTE (*Ann. Chim. Phys.* [6], **22**, 409—412).—See this vol., ii, 17.

Estimation of Cyanogen in Spent Materials from Gas Purifiers and in Illuminating Gas. By H. DREHSCHMIDT (*Chem. Centr.*, 1892, i, 1006—1008; from *J. Gasbeleucht. Wasserversorg.*, **35**, 221—226, 268—270).—*Estimation of Cyanogen in Spent Materials.*—A mixture of 10 grams of the spent material, about 150 c.c. of water, 1 gram of ammonium sulphate, and 15 grams of mercuric oxide are placed in a 500 c.c. flask and boiled for 15 minutes. After cooling, 0·5—1 c.c. of a saturated solution of mercurous nitrate is run in, and then ammonia is added until no further preciptate is formed. The flask is filled up to the mark, and an additional 8 c.c. of water, corresponding with the volume of the solid matter present, is added. After shaking thoroughly, the liquid is passed through a dry filter, and 200 c.c. of the filtrate (corresponding with 4 grams of the material) is placed in a 400 c.c. flask and treated with 7 grams of zinc dust and at least 6 c.c. of ammonia solution (sp. gr. 0·91). The mixture is shaken several times, 2 c.c. of 30 per cent. potassium hydroxide solution is added, and the liquid is made up to 401 c.c. and filtered through a dry filter. 100 c.c. of the filtrate (corresponding with 1 gram of the substance) is added to excess of N/10 silver nitrate solution contained in a 400 c.c. flask, the liquid is acidified with nitric acid, the flask filled up to the mark, and the solution again filtered. Finally, 200 c.c. of this last filtrate is titrated by Volhard's method with N/20 ammonium thiocyanate. The required quantity of this solution directly corresponds with the excess of silver, and by subtracting it from the total volume of silver solution employed, the amount of silver corresponding with cyanogen is obtained [1 c.c. 1/10 normal solution of silver nitrate = 0·002598 gram cyanogen (0·2598 per cent.) = 0·004771 gram Fe_7Cy_{18} (0·4771 per cent.).]

Under some conditions, for example, when compounds containing chlorine are present, mercurous nitrate cannot be satisfactorily employed, and the author then uses potassium iodide in its place. The titration is then complete as soon as the turbidity caused by silver

iodide is persistent, after repeated additions of 5—10 c.c. of 30 per cent. potassium hydroxide solution.

Estimation of Cyanogen and Hydrocyanic Acid in Illuminating Gas.—Potassium hydroxide alone is not a good absorbent of hydrocyanic acid, but when it contains ferrous hydroxide in suspension the absorption is complete. The author employs an absorption apparatus consisting of a wide cylinder fitted with a stopper with two holes. Through one of these the gas enters and passes to a small glass bell, from which it escapes through the absorbent liquid by a number of perforations on the upper side. To estimate the cyanogen, the gas is passed through two absorption cylinders, the first containing 15 c.c. of ferrous sulphate solution (1 : 10) and 15 c.c. of potassium hydroxide solution (1 : 3), and the second, 5 c.c. of ferrous sulphate solution, 5 c.c. of potassium hydroxide solution, and 20 c.c. of water. Under ordinary conditions, 100 litres of gas is employed, and it is allowed to pass through the apparatus at the rate of 60—80 litres per hour. The contents of the absorption-cylinders are made up to 250 c.c. and filtered. 200 c.c. of the filtrate is placed in a 300 c.c. flask, neutralised with an equivalent quantity of sulphuric acid, mixed with ammonium sulphate (2 grams) and mercuric oxide (15 grams), and boiled for 15 minutes. When cold, the bulk is made up to 301·3 c.c., the solution is filtered, and 250 c.c. of the filtrate is placed in a 300 c.c. flask with 6—10 c.c. of ammonia (sp. gr. 0·91) and 7 grams of zinc dust. After shaking thoroughly, 2 c.c. of potassium hydroxide is added, the solution is made up to 301 c.c., again shaken, and passed through a dry double filter paper. To 200 c.c. of the filtrate 30 c.c. of potassium iodide solution is added, and the resulting solution is titrated with N/20 silver solution, in the manner described above. If n is the silver required, the expression 2·598 n 9/4 gram gives the weight of cyanogen in 100 c.c. of the gas. G. T. M.

Estimation of Glycerol by Benedikt and Zsigmondy's Process. By C. Mangold (*Zeit. angw. Chem.*, 1891, 400—401).—The author has modified the process, and operates as follows:—0·4 gram of the sample is dissolved in a litre flask, in 300 c.c. of water containing 10 grams of potassium hydroxide, 55 c.c. of a 5 per cent. solution of potassium permanganate is slowly added, and the mixture allowed to remain for about half an hour. Solution of hydrogen peroxide is then added until the manganese is precipitated and the supernatant liquid looks quite colourless, after which water is added up to the mark, the whole thoroughly mixed, and 500 c.c. filtered through a dry filter. After boiling the filtrate in a flask for half an hour to destroy the excess of hydrogen peroxide, the liquid, which contains oxalic acid derived from the oxidation of the glycerol, is cooled to 60°, acidified with sulphuric acid, and titrated with permanganate. The test analyses are satisfactory. The presence of butyric acid does not interfere. L. de K.

Estimation of Inorganic Constituents in Sugars. By Alberti and Hempel (*Zeit. angw. Chem.*, 1891, 486—492).—The conventional sulphuric acid process, although convenient and safe, is really very

untrustworthy, particularly if the sample contains any sandy matter. The authors, who communicate the results of more than 200 experiments, now recommend the following process:—About 6 or 7 grams of coarsely powdered quartz is ignited in a 35 c.c. platinum dish, and after cooling, the whole is weighed. 5 grams of the sugar is now introduced, and after this is well mixed with the sand by means of a thin platinum wire, the dish is placed in a platinum muffle and ignited with a full flame. The sugar burns quietly without frothing. After half an hour, sometimes longer, the operation is finished, and the ash may be weighed. If dealing with molasses, about 3 grams of the sample is a convenient quantity to work on. The ash is free from carbonic acid, and as chlorides and sulphates are not decomposed by the heated silica, the true mineral matter of the sugar is obtained.

L. DE K.

Estimation of Sugar and Tannin in Wine. J. H. VOGEL (*Zeit. angw. Chem.*, 1891, 449).—The author (Abstr., 1891, 1557) states that by adopting Borntträger's plan, the decolorisation of very deeply coloured wines may be effected by a comparatively small quantity of basic lead acetate without interfering with the accurate estimation of the sugar; but he still uses, by preference, animal charcoal, which not only removes the colouring matter, but also any tannin.

L. DE K.

Estimation of Pentosans and Pentoses in Vegetables. By E. R. FLINT and B. TOLLENS (*Ber.*, **25**, 2912—2917).—Continuing their work on this subject (Abstr., 1892, 388), the authors have confirmed their previous results. They recommend the gravimetric estimation of the furfuraldehyde hydrazone as the most exact and convenient. Care must be taken that the quantity of sodium chloride in the 500 c.c. of neutralised distillate is always 81·5 grams (that is, the quantity of sodium chloride produced by the neutralisation of 400 c.c. of distillate containing 12 per cent. of hydrogen chloride). If the distillate is less than 400 c.c., 10·2 grams of sodium chloride is added for every 50 c.c. deficiency of distillate before neutralisation, addition of phenylhydrazine, and making up to 500 c.c. The following factors were determined:—

1. Arabinose = hydrazone × 1·229 + 0·0177.
2. Xylose = hydrazone × 1·031 − 0·001.
3. Pentose (average, if kind unknown) = hydrazone × 1·13 + 0·0083.
4. Furfuraldehyde = hydrazone × 0·516 + 0·0254.
5. Pentosan (araban or xylan) = pentose × 0·88.

The presence of starch or cane sugar interferes to some extent with the determination, causing rather too low numbers to be obtained. Cellulose does not appear to affect the results.

Günther's titration method (*loc. cit.*) gives rather too high results, owing to the levulinic acid, &c., which is usually present in the distillate also forming hydrazones. As those hydrazones are pretty soluble, they do not influence the gravimetric method.

The authors have determined the amounts of pentosans, &c., in a number of woods, gums, &c. L. T. T.

Estimation of Stachyose in the Tubers of Stachys tuberifera. By A. v. Planta and E. Schulze (*Landw. Versuchs-Stat.*, **41**, 123—129; compare Abstr., 1891, 1446).—It has been already shown that stachyose is by far the most prominent constituent of the sap of the tubers. The stachyose was first estimated with the polariscope; the washed and dried tubers were mashed, 250 grams quickly weighed, treated with lead acetate solution (20 c.c.) and alcohol (50 c.c.), and water added to make up to 800 c.c. When filtered, a portion was polarised in a 200 mm. tube. The results of this and a second experiment showed the percentage of stachyose to be 14·16 (14·2 and 14·13) in the fresh, and 73·07 per cent. in the dry tubers. A direct estimation in the expressed sap gave a percentage of 15·6. Attempts to determine the stachyose by treatment with hydrochloric acid and estimation of the glucose with Fehling's solution failed; acid of the strength required for inverting cane sugar was insufficient; with stronger acid, there is a danger of destroying a portion of the levulose formed.

The stachyose was next estimated as mucic acid after treatment with nitric acid. Weighed amounts of the powdered tubers were extracted with hot water, the extracts treated with slight excess of lead acetate, filtered, the filtrate treated with hydrogen sulphide, again filtered, and evaporated on the water-bath. The syrup was dissolved in nitric acid (sp. gr. 1·15), and evaporated at a gentle heat to about one-third of its bulk. 1 gram of stachyose (calculated from the polarimetric determination) required about 12 c.c. of nitric acid of the above sp. gr. The experiment was continued according to Tollens' method. The mean of the first two experiments was 63·3 per cent. of stachyose in the dry matter; the third experiment gave 61·6 per cent. That the results were lower than those obtained with the polariscope may be due to the presence of a second carbohydrate in the sap which is also dextrorotatory, but does not yield mucic acid when oxidised; or else the stachyose, when oxidised in presence of other substances, gives less mucic acid than when oxidised alone. It seems certain that it is not the first reason alone which caused the difference. The percentage obtained by polarisation is probably nearest the truth.

Besides stachyose, the tubers contain a second carbohydrate, which yields furfuraldehyde (1·98 per cent.) by de Chalmot and Tollens' method. It is concluded that the substance is a pentosan, that is, a carbohydrate which yields a pentose when treated with dilute acid. The amount in the dry tubers would be about 3·5 per cent. It is questionable whether it occurs in the sap. N. H. M.

Estimation of Acids in Beer. By Prior (*Chem. Centr.*, 1892, i, 767; from *Freie Verein. bayer. Vertreter. angw. Chem.*, **10**, 22—34).—The presence of secondary and primary phosphates in beer offers a great impediment to the determination of the free acids contained in it. Results, more satisfactory than those given by processes previously

described, are obtained as follows:—50 c.c. of the beer is freed from carbonic anhydride, and mixed, first with 150 c.c. of alcohol, then with 300 c.c. of ether. After remaining for 12 hours, the liquid is filtered, the ether is distilled off, and the alcoholic residue made alkaline with a known volume of N/10 sodium hydroxide solution. The alcohol is then distilled off, an equivalent quantity of N/10 sulphuric acid added, and the volatile acids distilled in a current of steam. The residue, after the distillation, contains only the free, non-volatile organic acids, together with a small quantity of acid phosphates and some neutral extractive matter. It is carefully titrated with alkali, and the neutral solution mixed with clean sea-sand and evaporated to dryness. The residue is treated with a quantity of N/10 sulphuric acid equivalent to the alkali recently added, heated on a water-bath and, after cooling, rinsed into a flask with 50 c.c. of alcohol and then mixed with 100 c.c. of ether. This treatment completely separates the organic acids from the phosphates. After evaporation of the alcohol and ether at the lowest possible temperature, the extract is titrated; whilst the sandy residue is also titrated in aqueous solution; the precipitate obtained on first adding alcohol and ether to the beer being treated in a similar way, so that the sum of both titrations gives an expression for the primary phosphates contained in the beer. The remainder of the acid phosphate, which goes into solution, is very small in comparison with the total quantity of phosphates.

Experiments show that it is most difficult to separate the acetic acid contained in beer in a satisfactory way. In order to estimate lactic acid and succinic acid in a mixed aqueous solution, they were carefully titrated with calcium hydroxide solution, evaporated to dryness, and digested with 90—98 per cent. alcohol. After 24 hours, the calcium succinate was collected, ignited and weighed as calcium oxide, and the amount of lactic acid present calculated by difference. No perfect method of estimating these acids in beer has yet been suggested. G. T. M.

Estimation of Succinic Acid. By A. Rau (*Chem. Centr.*, 1892, ii, 155—157; from *Revue Hygiène*, **14**, 225—242).—See this vol., i, 11.

Estimation of Citric Acid in Wine. By A. Klinger and A. Bujard (*Zeit. angw. Chem.*, 1891, 514—515).—The authors recommend the following process, which they use in preference to the one adopted by Nessler and Barth, as there is less danger of mistaking calcium malate for citrate. 250 c.c. of the wine is evaporated to about 80 c.c., acidified with acetic acid, and after adding some potassium acetate, mixed with 160 c.c. of strong alcohol. After 24 hours, the liquid is filtered, and the residue rinsed with a few c.c. of dilute spirit to redissolve traces of potassium citrate. The filtrate is then at once precipitated with basic lead acetate; the precipitate is collected on a filter, washed with dilute alcohol, and then decomposed by hydrogen sulphide in the usual manner.

The filtrate from the lead sulphide is concentrated and made slightly alkaline with milk of lime. After a few hours, the liquid is

filtered from any traces of calcium tartrate and phosphate. The filtrate is acidified with acetic acid and evaporated to dryness. The residue is dissolved in water with addition of a little hydrochloric acid, a little ammonium chloride is added, and after adding excess of ammonia, the whole is continually boiled. Any precipitate can now only be calcium citrate, as the malate is soluble in a boiling solution of ammonium chloride. L. DE K.

Estimation of Milk Fat with Demichel's Lactobutyrometer. By L. GRAFFENBERGER (*Landw. Versuchs-Stat.*, **41**, 43—54). Demichel's lactobutyrometer is constructed on the same principle as Marchand's, but differs from it in having a narrow tube for reading off the amount of fat, the fat being raised into this tube by the addition of water through a second tube (compare *Milchzeit.*, No. 23, 1891). The tube is graduated from 12·6 to 70. The method is as follows:—10 c.c. of milk is poured from a pipette into the apparatus, 2 drops of alkali solution, 10 c.c. of ether, and 10 c.c. of alcohol added, and the whole violently shaken. The apparatus is placed in water at 40° for 10 minutes, and then so much water added that the lower surface of the fat layer corresponds with the 12·6 mark; the amount of fat is then read off, the numbers showing the amount, in grams, in 1 litre of milk. The addition of water has to be made with great care, otherwise a part of the fat will again mix with the water. It is also very difficult in adding water to get the lower surface of the fat to correspond with the mark, and it would be preferable, instead of having the degrees marked on the glass, to have them on a movable metallic sheath, which could always be so placed as to correspond with the layer of fat. With regard to the method itself, it was found that aqueous potash (sp. gr. = 1·27) was of a suitable strength. The alcohol should be 91—92 per cent.; 40° is a better temperature for the separation than 20° (recommended by Tollens and Schmidt), but the amount of fat should be read off at 20°, after an interval of 30 minutes, as during the cooling there is a further separation of fat.

A number of results obtained by this method are given, together with results obtained by Soxhlet's method. Most of the results are very near the truth, but single estimations have little value. Averages of several results are, however, to be trusted; the averages obtained by the author differed only 0·1—0·2 per cent. from the Soxhlet results. By excluding such results as differ most from the others, averages were obtained which differed only 0·02—0·06 per cent. from Soxhlet's. The results were obtained after ascertaining the value of the calibration, calculating the divisions to $\frac{1}{10}$ c.c., and then the amount of fat by means of Schmidt and Tollens' table. It would be better to give up the empirical division on the Demichel apparatus, and to employ a scale showing $\frac{1}{10}$ c.c.

Although not at all equal to Soxhlet's, as regards accuracy, the Demichel apparatus is worthy of consideration, owing to the ease with which it is employed and its cheapness; but, on no account should the apparatus, as now made, be used without a previous comparison of the results it gives with those obtained either by a Soxhlet apparatus or gravimetrically. N. H. M.

Melting Point and Composition of Butter from Cows variously fed. By A. Mayer (*Landw. Versuchs-Stat.*, **41**, 15—35). —See this vol., p. 28.

Testing Linseed Oil Varnish. By W. Fahrion (*Zeit. angw. Chem.*, 1891, 540).—It is sometimes useful to know the state of oxidation of a linseed oil varnish. The process to be described is based on the fact, first noticed by the author, that the unsaturated fatty acids, on oxidation, yield compounds which are insoluble in light petroleum, and may in this manner be separated from the saturated fatty acids or their oxy-products.

The analysis is carried out as follows:—About 3 to 5 grams of the varnish is weighed out and saponified by means of 15 to 25 c.c. of an 8 per cent. alcoholic potash. After the spirit has been completely expelled, the soap is dissolved in 50—70 c.c. of hot water, and then transferred to a half-litre separating funnel. After decomposing the soap by means of hydrochloric acid, and subsequent cooling, the whole is shaken with 100 c.c. of light petroleum, and allowed to remain for about an hour. The aqueous liquid is now completely drawn off, and if any oxy-acids are present these will be found adhering to the sides of the funnel. The clear petroleum layer is carefully drawn off, and, after washing two or three times with light petroleum, the oxy-acids are dissolved in a little hot alcohol, and transferred to a weighed dish. After expelling the alcohol, the residue is finally dried for an hour at 100—105°.

The amount of oxy-acids found by the author in various samples of linseed oil varnish varied from 0·6 to 31·6 per cent. L. de K.

Estimation of Aniline, Methylaniline, and Dimethylaniline. By F. Reverdin and C. de la Harpe (*Bull. Soc. Chim.* [3], **7**, 211—212).—See this vol., i, 24.

Analysis of Linseed Cake. By A. Haselhoff (*Landw. Versuchs-Stat.*, **41**, 54—72; and by F. J. van Pesch, *ibid.*, 73—93).—See this vol., ii, pp. 39, 40).

Detection of Cochineal in Sausages. By A. Klinger and A. Bujard (*Zeit. angw. Chem.*, 1891, 515—516).—20 grams of the cut up sausage is heated in a water-bath with a mixture of equal parts of water and glycerol. If any carmine is present, the liquid gets decidedly reddish, but in its absence only a slight yellow colour is noticed. The solution is filtered, and, if necessary, heated with another 20 grams of the sample. The clear liquid, which is, of course, free from fatty matter, is then examined in the spectroscope, when any carmine will be readily recognised by its characteristic absorption bands. Or the colouring matter may be precipitated as a lake, and this, after washing, may be dissolved in a little tartaric acid. In this way a more concentrated solution of the colouring matter is obtained, and the spectroscopic test is consequently more satisfactory.

L. de K.

General and Physical Chemistry.

Molecular Refractive Power of Organic Compounds for Infinite Wave-length. By H. LANDOLT and H. JAHN (*Zeit. physikal. Chem.*, **10**, 289—320).—From measurements for electrical waves of great wave-length, it has been shown that Maxwell's relation, $n^2 = k$, between the index of refraction and the dielectric constant is true for a considerable number of solid and liquid substances. The authors have determined this constant for several series of organic substances and have introduced it into Lorentz's formula, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$, in order to determine the specific refraction equivalents for infinite wave-length. The accompanying table gives the values of $\sqrt{k}$ and of A, the first constant of Cauchy's dispersion formula, which should also be equal to n for substances of normal dispersion.

	$\sqrt{k}$.	A.
Hexane	1·3608	1·3683
Octane	1·3899	1·3902
Decane	1·4015	1·4001
Amylene	1·4836	1·3750
Octylene	1·4758	1·4030
Decylene	1·4764	1·4246
Benzene	1·4816	1·4777
Toluene	1·5410	1·4743
Ortho-xylene	1·6101	1·4838
Metaxylene	1·5322	1·4755
Paraxylene	1·4942	1·4744
Ethylbenzene	1·5543	1·4756
Propylbenzene	1·5333	1·4703
Isopropylbenzene	1·5417	1·4718
Mesitylene	1·5157	1·4741
Pseudocumene	1·5462	1·4835
Isobutylbenzene	1·5309	1·4742
Cymene	1·4948	1·4712
Methyl alcohol	5·496	1·3216
Ethyl „	5·248	1·3527
Propyl „	4·629	1·3762
Isobutyl „	4·287	1·3865
Isoamyl „	4·041	1·3978

From the table it appears that only the paraffins have normal dispersion, and that the alcohols in especial are very anomalous. The following values of k were also determined.

Ethylene chloride	11·315
Ethylidene chloride	10·861
Methyl acetate	8·0165
Ethyl acetate	6·7381
Propyl acetate	6·639
Isobutyl acetate	5·6808
Amyl acetate	5·0695
Ethyl formate	9·102
Propyl formate	9·0163
Isobutyl formate	7·2801

The temperature of experiment ranged from 0° to 23°. J. W.

Infra-Red Emission Spectrum of the Alkalis. By B. W. Snow (*Ann. Phys. Chem.* [2], **47**, 208—251).—The infra-red spectrum of the electric arc into which salts of the alkalis were introduced was investigated by means of a sensitive bolometer, constructed of two fine Wollaston platinum wires, one of which was flattened and exposed to the different parts of the spectrum in succession. As the exposed surface of the bolometer was very small ($1\frac{1}{3}$ sq. mm.) a very sensitive galvanometer had to be employed, details of the construction of which are given in the paper. A flint glass prism of strong dispersion was used to produce the spectrum. An investigation of the spectrum of the electric arc itself showed that the maximum of energy (measured by the deflection of the galvanometer) lay further out towards the violet than the Fraunhofer lines H_1 and H_2, namely, from $\lambda = 0{\cdot}385\mu$ to $\lambda = 0{\cdot}388\mu$. In order to get the alkali salts (chlorides) introduced into the arc, both the carbon poles, 8 mm. in diameter, were drilled out axially and the boring was then filled with the salt under examination. The diameter of the hole in the positive (lower) carbon was 3 mm., in the negative carbon 1·5 mm. With this arrangement, the carbon spectrum is totally destroyed and the pure metal spectrum takes its place.

The results obtained are exhibited in tabular and in curve form. All the alkali metals were investigated. In the case of lithium and sodium, the wave-lengths of the lines observed agree well with those calculated by Kayser and Runge. With the other metals, there are considerable discrepancies. J. W.

Electromotive Force of Oxidation Cells. By W. D. Bancroft (*Zeit. physikal. Chem.*, **10**, 387—409).—Two test tubes, one containing an oxidising solution, the other a reducing solution, had their contents electrolytically connected with each other by means of side-tubes and an inverted siphon filled with a solution of sodium chloride. Electrodes of platinum, cut from the same piece of foil, were immersed in the liquids and the electromotive force between them measured by means of the galvanometer, a Latimer-Clark cell being used as standard. In all, 17 oxidising solutions and 24 reducing solutions were examined. The usual concentration was $\frac{1}{3}$ normal, and the temperature of experiment varied from 16° to 18°.

The results arrived at by the author are as follows. The electro-

motive force of oxidation cells is an additive property, that is, it is equal to the sum of two terms, one depending on the nature of the oxidising agent and the other on the nature of the reducing agent. It is independent of the nature of the electrodes, if these are not attacked, and is also (within wide limits) independent of the concentration of the solutions. The nature of the solution which effects the electrolytic connection is without influence on the electromotive force. A free acid is a stronger oxidising agent than its alkaline salts; the converse holds true for reducing agents. Under these restrictions, the electromotive force is, in general, independent of the nature of the indifferent ions. The electrodes are not always non-polarisable, as theory requires; but the variations may usually be attributed to secondary influences. J. W.

Electrolytic Conductivity and Dissociation. By J. Brown (*Phil. Mag.* [5], **33**, 82—89).—The electrolytic dissociation theory and Arrhenius and Claisen's theory of electrolytic conductivity from which it is derived are adversely criticised by the author, in the sense that neither is requisite to explain known facts. J. W.

Specific Heat of the Atoms and their Mechanical Constitution. By G. Hinrichs (*Compt. rend.*, **115**, 239—242).—If m is the mass of an elementary atom and v its velocity of maximum vibration, and M the mass of any compound radicle composed of n atoms of m and with a velocity, V, round its centre of gravity, $2E' = \Sigma mv^2 + MV^2$, where E′ is the total energy of vibration. But also $MV^2 = 2k\mathrm{T}$ and $mv^2 = 2\rho k\mathrm{T}$, where k and ρ are constants and T the absolute temperature, so that $E' = k(1 + \rho n)\mathrm{T}$. The specific heat due to the vibrations of the atoms will then be $s' = \frac{dE'}{d\mathrm{T}} = k(1 + \rho n)$. This formula shows that the specific heat of the compound radicle increases with the number n of the elementary atoms which it contains. For elementary substances, the atomic heat will be independent of n, and therefore constant. In this case ρ will be nothing, or the independent velocity of vibration of the particles composing m will be nothing. That is to say, in compound substances or radicles, the constituent elemental atoms possess their own peculiar motion of vibration, but in elementary substances the constituent atoms are incapable of individual vibration. It is therefore not surprising that hitherto all efforts at decomposing elementary substances have failed. H. C.

Heat of Combustion of Organic Compounds. By F. Stohmann (*Zeit. physikal. Chem.*, **10**, 410—424).—The author continues the tabulation of the heats of combustion of organic compounds in the manner previously described (Abstr., 1891, 251). Data for nearly 300 compounds are given, the following classes being represented:—hydrocarbons, alcohols, carbohydrates, phenols, camphor-derivatives, phenol ethers, aldehydes, acids, anhydrides, lactones, lactonic acids, ketones, ethereal salts, amides, amido-acids, amines, azo-compounds, nitro-compounds, proteïds, chloro-compounds, and hydrochlorides. J. W.

Constitution of Phosphoric Acid and the Thermal Value of its three Acid Functions. By DE FORCRAND (*Compt. rend.*, **115**, 610—613).—The heat of dissolution of anhydrous mono-sodium phosphate is −0·13 Cal. at 20°, and combining this result with the results of previous investigators of the thermal behaviour of phosphoric acid, it follows that:—

H_3PO_4 sol. + Na sol. = H gas + NaH_2PO_4 sol.	develops	+ 60·60 Cal.
NaH_2PO_4 sol. + Na sol. = H gas + Na_2HPO_4 sol.	„	+ 49·20 „
Na_2HPO_4 sol. + Na sol. = H gas + Na_3PO_4 sol.	„	+ 38·33 „
H_3PO_4 sol. + Na_3 sol. = H_3 gas + Na_3PO_4 sol.	„	+148·13 „

The total thermal value of the three acid functions of phosphoric acid is +148·13 Cal. and the mean value of each function is +49·38 Cal. The apparent value of the first function, however, is +60·60 Cal., and of the third only +38·33 Cal. These results agree with the supposition that phosphoric acid has the constitution $PO(OH)_3$, and its molecule is symmetrical in the same manner as the molecule of sulphuric acid, glycol, or pyrogallol. The value of the first acid function is exaggerated by the occurrence of intramolecular combinations between the unsaturated acid functions, similar to those already observed by the author in the case of polyhydric alcohols and phenols, and the apparent value of the third acid function is lower, because of the absorption of energy required to break up these intramolecular combinations before the acid can be completely saturated.

C. H. B.

Temperature of Maximum Density of Aqueous Solutions. By L. DE COPPET (*Compt. rend.*, **115**, 606—607).—Despretz, in 1839, formulated a law for the reduction of the point of maximum density of water which is similar to that of Blagden for the reduction of the freezing point, and states that the reduction of the temperature of maximum density below 4° is proportional to the weight of substance dissolved in 100 parts of water. The author is now able, as a result of his own observations, to bring the laws for the reduction of the maximum density into further accordance with those for the reduction of the freezing point, and to state that substances of similar composition, and in some cases of very different composition, have the same molecular reduction of the temperature of maximum density. This law obtains within the same limits to which the law of the reduction of the freezing point applies. Only one exception has, up to the present, been found, and this is in the case of solutions of ethyl alcohol and water, as mixtures of the two behave abnormally with respect to the reduction of the freezing point (see next abstract).

An interesting relation exists between the reduction of the freezing point C and that of the temperature of maximum density D. Substances generally may be divided into three groups according to the values of the ratio D/C. In the first group, at present comprising

potassium hydroxide, oxalic acid, the chlorides of sodium, potassium, and calcium, and potassium iodide, the value of this ratio is about 4. In the second group, containing sugar, and the carbonates and sulphates of the alkali metals, the value is from 7 to 8. In the third group, of which copper sulphate is as yet the only representative, the value is from 11 to 12. The three values for the ratio D/C are, therefore, as will be seen, themselves approximately in the proportion 1 : 2 : 3. H. C.

Temperature of Maximum Density of Mixtures of Alcohol and Water. By L. de Coppet (*Comp. rend.*, **115**, 652—653).—In a former paper (preceding abstract), the author pointed out that solutions of alcohol in water do not obey the law which he has formulated for the reduction of the temperature of maximum density. The following table, compiled from his own observations and those of Despretz and Rossetti, illustrates the abnormal behaviour of alcohol in this respect :—

M.	C.	D.	$\frac{C}{M}$.	$\frac{D}{M}$.
0·09	0·00°	− 0·12°	0·000	−1·333
0·642	0·27	− 0·16	0·421	−0·249
1·346	0·54	− 0·29	0·401	−0·215
2·568	1·03	− 0·39	0·401	−0·152
3·943	1·57	− 0·02	0·398	−0·005
6·21	2·63	+ 0·83	0·424	+0·134
6·575	2·60	+ 1·15	0·395	+0·175
7·408	2·83	+ 1·75	0·382	+0·236
8·46	3·54	+ 2·18	0·418	+0·258
10·80	4·45	+ 4·19	0·412	+0·388
17·12	7·47	+12·48	0·436	+0·729

The first column contains the weights of alcohol in 100 grams of water, the second the reduction of the freezing point, the third the reduction of the temperature of maximum density, and the fourth and fifth the numbers in the second and third columns divided by those in the first. It will be seen that although the solutions obey Blagden's law with regard to the reduction of the freezing point, the reduction of the temperature of maximum density is not proportional to the quantity of alcohol present. Indeed, for dilute solutions, there is an actual rise instead of a fall in the temperature of maximum density. H. C.

Density and Composition of Sulphuric Acid Solutions. By A. W. Rücker (*Phil. Mag.* [5], **33**, 204—209; compare Abstr., 1892, 271—272).—This paper is a continuation of the discussion between the author and Pickering as to the use of the bent lath in detecting changes of curvature in curves representing experimental data. The author states his position with regard to the density curve for sulphuric acid at 18° as follows :—"Any peculiarity in a curve on which

argument is founded must be proved to be outside the error of experiment. No weight can be attached to a representation which is not unique in the sense that no other is compatible with the observations when all allowance is made for experimental error. Mr. Pickering's first solution (the four-break one) is not unique. He has himself offered another (one break), and I have contributed a third (no breaks). . . . Put briefly, the observations, accurate and numerous as they are, are not accurate enough, and not numerous enough, to decide whether the 18° density curve is, or is not, discontinuous between 47 per cent. and 80 per cent." J. W.

Dissociation Measurements of Feebly Dissociated Acids. By J. E. TREVOR (*Zeit. physikal. Chem.*, **10**, 321—353).—It has been shown by Arrhenius that the rate of inversion of sugar by acids is, *cæteris paribus*, proportional to the concentration of the hydrogen ions in the solution. This rate increases very rapidly with the temperature, so that at 100° it is possible to measure, by this means, the amount of hydrogen ions produced by the dissociation of a very feeble acid when other methods fail. The author has worked out the method for high temperatures, and gives a detailed description of the apparatus employed. The substances chiefly studied were the hydrogen sodium salts of the oxalic acid series.

From his observations, the author draws the following conclusions:—

The inversion constant, which corresponds with total inversion, is 17·92 at 100°.

The percentage increase of the inversion constant per degree rise of temperature is the same, or nearly the same, for all acids in a given range of temperature.

The electrolytic dissociation of organic and inorganic acids is, in general, almost independent of the temperature, at least between 25° and 100°.

The dissociation of hydrogen from the acid salts of the bibasic organic acids is relatively small, sinking as low as 0·03 per cent. for the higher members of the series at a dilution of 32, and seldom reaching 1 per cent. at a dilution of 256. The dissociation of these substances follows the same law in all cases, the degree of dissociation being nearly proportional to the dilution, instead of to the square root of the dilution as is the case for the acids themselves. When the acid salts are arranged in order of the amount of dissociation of hydrogen at a given dilution, this order is the same as that of the dissociation constants of the free acids themselves. J. W.

Diffusion of Oxygen and Nitrogen in Water. By C. DUNCAN and F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, **17**, 147—164).—A tube was first emptied, then filled with boiled water. This was exposed to the action of the atmosphere for varying periods, and the gases absorbed pumped off and analysed. Daily observations on barometric pressure and temperature were made. The total amount of gas absorbed increased with the duration of the exposure; the daily increment in the amount absorbed, however, gradually diminishes.

The results are given in extensive tables for oxygen, nitrogen, and carbonic anhydride at different depths below the surface. From the results, the conclusion is drawn that in the great depths of the sea or lakes, animals, if they live, either require less oxygen, or that the gaseous exchange between the water and the atmosphere is carried out by other means than diffusion. (See this vol., ii, 81.)

W. D. H.

Van der Waals' Corresponding States. By S. Young (*Phil. Mag.* [5], **33**, 153—185).—In a series of tables and curves, the author gives the critical constants, corresponding temperatures and pressures, molecular volumes in corresponding states, and various ratios between these magnitudes, for different substances. Benzene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, carbon tetrachloride, stannic chloride, ether, methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid form the material studied by the author.

Van der Waals' statement that, "if the absolute temperatures of various substances are proportional to their absolute critical temperatures, their vapour pressures will be proportional to their critical pressure," proves not to be true except in a very limited number of cases, and occasionally it is very wide of the mark. From this, it follows that in the comparison of molecular volumes, the ratios at corresponding pressures must differ from those at corresponding temperatures. The deviations of the molecular volumes of liquids are smaller than the deviations in any of the other cases, but still not within the limits of experimental error. The comparisons at corresponding pressures are somewhat better than at corresponding temperatures. In the case of the molecular volumes of saturated vapours at corresponding pressures, the deviations from constancy are within the limits of experimental error for ether and stannic chloride, and are relatively small for benzene and carbon tetrachloride.

When the alcohols, which differ widely from the other substances studied, are compared amongst themselves, the deviations are much smaller than before, but still far outside the error limit.

Double molecules of acetic acid probably exist even at the critical temperature.

The author gives details of the manner of determining the critical volumes of the various substances, and discusses some relations advanced by himself and by Guye.

J. W.

Method of Measuring Loss of Energy due to Chemical Union, &c. By G. Gore (*Phil. Mag.* [5], **33**, 28—53; compare Abstr., 1892, 257, 930).—The author measures the electromotive force of a voltaic couple consisting of platinum and of another metal (usually aluminium, tin, cadmium, zinc, or magnesium), immersed in two solutions separately, and then in the solution resulting on mixing the two. He gives the following sketch of his method:—Take a known quantity of an acid dissolved in a known weight of water, and measure the electromotive force A developed by a small couple of platinum and aluminium immersed in the solution. Take a chemically equivalent quantity of a base dissolved in the same

weight of water, and find the electromotive force B developed by the same element. Again, ascertain the electromotive force C in an equivalent solution of the salt resulting from the combination of the acid and base. Multiply A into the equivalent weight of the acid, B into that of the base, and divide the sum of the products by the sum of the equivalents: call the quotient D. Subtract C from D and multiply by $100/D$. The percentage loss or gain of electromotive force thus obtained represents in the author's opinion the relative amounts of loss or gain of molecular energy which have occurred on the union of the acid and base.

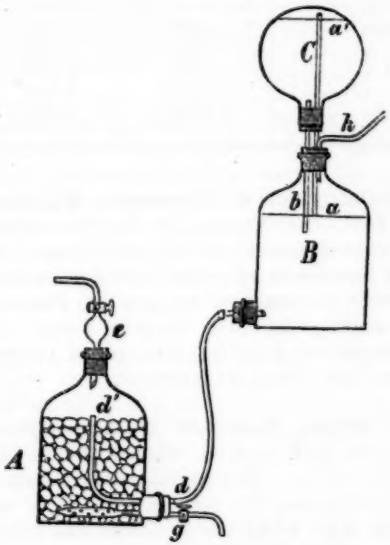
The results of numerous experiments with various classes of substances are given in tabular form. When an acid and base neutralise each other, there is in almost all cases an increase of electromotive force. There is an increase in about four-fifths of the cases in which a carbonate is used to neutralise an acid. Very little change in the electromotive force is observed when salt solutions or acid solutions are mixed. Salts, on the other hand, when mixed with acids, show considerable changes.

Most of the solutions investigated contained 1 equiv. of substance dissolved in 100 mols. of water. J. W.

Use of certain Colouring Matters for the Determination of Affinities. By W. Spitzer (*Pflüger's Archiv*, **50**, 551—573).—It has been noticed that the neutral and many acid salts of organic acids have an alkaline reaction towards lacmoïd, so that obviously a division of the alkali between the organic acid and the lacmoïd takes place. It may be assumed that this division will follow the Guldberg-Waage law of mass action, and will depend on the relative affinities of the acid and the lacmoïd for the alkali, so that by comparing the affinities of different acids with that of lacmoïd, it should be possible to obtain relative numbers for the affinities of the acids themselves. This the author has done for a number of organic acids, and obtained results which are in very fair accordance with those calculated from Ostwald's experiments on the affinities of the same acids, determined by their rate of hydrolysis of cane sugar and of methyl acetate, and by the electrical conductivities. The above method, therefore, may be regarded as leading to correct results. The importance of a knowledge of the affinities of the organic acids for a correct interpretation of those physiological changes in which such acids take part is pointed out. H. C.

Rate of Evaporation of Solutions of Sodium and Potassium Chlorides. By P. Lesage (*Compt. rend.*, **115**, 473).—The author finds by direct experiment that pure water evaporates more rapidly than aqueous solutions of sodium or potassium chloride, and that solutions of potassium chloride evaporate more rapidly than solutions of sodium chloride of the same concentration. These results agree with Wüllner's determinations of the vapour pressures of these liquids. C. H. B.

A Continuous Gas Evolution Apparatus. By A. v. KALECSINSZKY (*Zeit. anal. Chem.*, **31**, 544—548).—The modifications in the principle of Deville's and Kipp's apparatus are that the acid which has once passed from the reservoir *B* into the generator *A* becomes there fully neutralised, and can never be driven back into the reservoir, but is drawn off at the tap *g*, so that the acid when it is



brought into contact with the solid reagent is always fresh and of full strength. Further, the use of the Marriotte's flask *C* maintains the level of the acid in *B*, and the resulting pressure, constant. Any gas evolved after the tap *e* is closed escapes through *B* and by *h*, which should, therefore, be carried into a chimney. M. J. S.

Inorganic Chemistry.

Vapour Density of Halogen Hydrides at Low Temperatures. By H. BILTZ (*Zeit. physikal. Chem.*, **10**, 354—362).—It has been repeatedly shown that the vapour density of hydrogen fluoride at low temperatures (below 26°) corresponds with the molecular formula H_2F_2, and not with the simple formula HF. In order to ascertain if the same tendency to the formation of double molecules exists in the corresponding halogen compounds, the author has determined their vapour density at low temperatures, using the

apparatus of V. Meyer and Goldschmidt (*Ber.*, **15**, 1161), with slight modifications. His results show that no such tendency exists.

	Temperature.	Vapour density.	
		Found.	Calculated for HX.
Hydrogen chloride	−77°	1·197	1·258
Hydrogen bromide	−15	2·989	2·770
" "	−28	2·873	"
Hydrogen iodide	−17	4·569	4·423
" "	−25	4·619	"

J. W.

Oxidation of Solutions of Hydrogen Sulphide. By SALAZAR and NEWMANN (*Bull. Soc. Chim.* [3], **7**, 334—336).—The authors' experiments show, in opposition to those of Lindo (Abstr., 1888, 750), that solutions of hydrogen sulphide in the mixture of glycerol and water (equal parts), proposed by Lepage (*J. Pharm.*, 1867), undergo less change on keeping than do those in water. Furthermore, the oxidation of hydrogen sulphide in solutions of the gas proceeds more rapidly in diffused light than in darkness. A. R. L.

Influence of Nitric Peroxide on the Specific Gravity of Nitric Acid. By G. LUNGE and L. MARCHLEWSKI (*Zeit. angw. Chem.*, 1892, 10—12; 330—331).—The authors have found that the results obtained when determining the strength of nitric acid by its specific gravity will be too high when the acid contains nitric peroxide. They have now constructed tables which give the corrected specific gravity when the amount of nitric peroxide is known. This is best estimated by delivering the nitric acid from a burette into a standard solution of potassium permanganate until the latter is quite decolorised.

When titrating nitric acid which contains nitrous acid, using methyl-orange as indicator, the latter should not be added until the acid is practically neutralised. L. DE K.

Behaviour of Nitric Oxide at High Temperatures. By F. EMICH (*Monatsh.*, **13**, 615—622; compare Abstr., 1892, 940).—After discussing a question of priority, the author describes an apparatus he employs for determining to what extent decomposition occurs when nitric oxide is heated at various temperatures in porcelain tubes. Langer and Meyer's statement, that nitric oxide remains unchanged when heated at 900° and 1200°, is shown to be an error. In fact, as stated by Berthelot (*Compt. rend.*, **77**, 1448), decomposition occurs when the gas is heated to a feebly glowing heat, such as will cause the containing tube to appear red in a darkened room.

G. T. M.

A Crystallised Compound of Arsenious and Sulphuric Anhydrides. By R. PEARCE (*Zeit. Kryst. Min.*, **20**, 632; from *Proc. Colorado Sci. Soc.*, **3**, 255—256).—In 1868, the author described

a crystallised compound of arsenious and sulphuric anhydrides derived from a calcining kiln in Swansea. Since then he has observed the same compound at the Argo Smelting Works in Colorado. It occurred some 3 feet under the uppermost part of the hearth in fine groups of large crystals encrusting lumps of slag. The crystals are of a complicated form, apparently monoclinic, with a pearly to adamantine lustre, a white colour, and a perfect cleavage. Analysis yielded:—

As_2O_3.	SO_3.	SiO_2 and loss.	Total.
68·22	28·91	2·87	100·00

B. H. B.

Carbonic Anhydride in the Air. By A. Petermann and J. Graftiau (*Chem. Centr.*, 1892, ii, 201).—The amount of carbonic anhydride has been determined daily during two years in the air taken from the open country near Gemploux, a small Belgian town. In the average, it is 2·944 vols. per 10,000; in the town itself 3·70. It was estimated by aspirating the air through standard baryta, and determining the excess of the latter by means of oxalic acid. The amount of carbonic anhydride present is not affected by the direction of the wind, or by its blowing off the sea or from the land. Rain, quantity of moisture in the air, ordinary variations of temperature (from $-5°$ to $+25°$) and pressure, and the change of season, are equally without effect. Mist and snow, however, produce an increase; so does an unusual barometric depression, especially when accompanied by a strong sea breeze and a very low temperature; a very high temperature produces a diminution. C. F. B.

Rubidium and Potassium Trihalides. By H. L. Wells and H. L. Wheeler (*Amer. J. Sci.* [3], **43**, 475—487).—The discovery of a series of cæsium trihalides (Abstr., 1892, 773), has led the authors to investigate the analogous rubidium and potassium compounds. The following table gives a list of the salts which they have been able to prepare, together with a list of the cæsium series for comparison:—

CsI,I_2,	RbI,I_2,	KI,I_2,
$CsBr,I_2$,	—	—
$CsBr,BrI$,	$RbBr,BrI$,	KBr,BrI,
$CsCl,BrI$,	$RbCl,BrI$,	—
$CsCl,ClI$,	$RbCl,ClI$,	KCl,ClI,
$CsBr,Br_2$,	$RbBr,Br_2$,	—
$CsCl,Br_2$,	$RbCl,Br_2$,	—
$CsCl,ClBr$.	$RbCl,ClBr$.	—

The compound KI,I_2 had been previously obtained by G. S. Johnson (this Journal, 1877, i, 249). The failure to prepare the one member lacking in the rubidium series is due, no doubt, to the comparative instability of this series. In the potassium series only those salts could be prepared which correspond with the more stable cæsium and rubidium compounds. The authors describe in considerable detail the method of preparation of these compounds, and discuss their

colour, stability, fusibility, and behaviour with solvents, whilst their crystallography is fully described in an appendix by S. L. Penfield.

B. H. B.

Pentahalides of the Alkali-metals. By H. L. Wells and H. L. Wheeler (*Amer. J. Sci.* [3], **44**, 42—49).—From the peculiar behaviour of cæsium tribromide and tri-iodide observed in their previous investigations, the authors concluded that a still higher bromide and iodide existed. These they have now identified as pentahalides. A description is given of the methods adopted for preparing the following compounds:—CsI_5, $CsBr_5$, $CsCl,Cl_2I$, $RbCl,Cl_2I$, KCl,Cl_2I, $NaCl,Cl_2I + 2H_2O$, and $LiCl,Cl_2I + 4H_2O$. The crystallography of these compounds is described by S. L. Penfield. The compound KCl,Cl_2I was described in 1839 by Filhol. The sodium and lithium analogues of this compound differ from all the other polyhalides studied by the authors inasmuch as they contain water of crystallisation.

B. H. B.

Cæsium and Rubidium Aurochlorides and Aurobromides. By H. L. Wells and H. L. Wheeler (*Amer. J. Sci.* [3], **44**, 157—162).—The compounds that have been prepared are $CsAuCl_4$, $2CsAuCl_4 + H_2O$, $CsAuBr_4$, $RbAuCl_4$, and $RbAuBr_4$. Their study was undertaken in the hope that some crystallographic analogy might exist between them and the alkali pentahalides described by the authors. No such analogy has been found; but, as some of these gold salts have never been described, an account is given of their preparation, properties, methods of analysis, and, in an appendix by S. L. Penfield, of their crystallography.

B. H. B.

Cæsium and Rubidium Iodates. By H. L. Wheeler (*Amer. J. Sci.* [3], **44**, 123—133).—The author has prepared the following new compounds:—

$RbIO_3$,	$CsIO_3$,
$RbIO_3,HIO_3$,	$2CsIO_3,I_2O_5$,
$RbIO_3,2HIO_3$,	$2CsIO_3,I_2O_5,2HIO_3$,
$RbCl,HIO_3$,	$CsCl,HIO_3$.
$3RbCl,2HIO_3$.	

The method of analysis adopted is described, and crystallographical descriptions of the various compounds are furnished by S. L. Penfield.

The results of the investigations of the rubidium salts show that the normal iodate is the only one of the series that can be recrystallised unaltered from an aqueous solution. In the case of the cæsium salts, the normal iodate and the salt $2CsIO_3,I_2O_5$ are not decomposed by water. The latter salt, and not the normal iodate, is given by the other cæsium salts when recrystallised from water.

B. H. B.

Cæsium-Mercury Halides. By H. L. Wells (*Amer. J. Sci.* [3], **44**, 221—236).—After enumerating all the previously-described mercury double halides containing the alkali metals or ammonium, the author describes the mode of preparation of the following salts:—

I.	II.	III.
Cs_3HgCl_5,	Cs_2HgCl_4	$CsHgCl_3$,
Cs_3HgBr_5,	Cs_2HgBr_4,	$CsHgBr_3$,
Cs_3HgI_5,	Cs_2HgI_4,	$CsHgI_3$,
$Cs_3HgCl_3Br_2$,	$Cs_2HgCl_2Br_2$,	$CsHgClBr_2$,
$Cs_3HgBr_3I_2$.	$Cs_2HgBr_2I_2$,	$CsHgBrI$.
	$Cs_2HgCl_2I_2$.	

IV.	V.	VI.
	$CsHg_2Cl_5$,	$CsHg_5Cl_{11}$,
	$CsHg_2Br_5$,	
$Cs_2Hg_3I_8$.	$CsHg_2I_5$,	
	$CsHg_2ClBr_4$.	$CsHg_5ClBr_{10}$.

One of these compounds, Cs_2HgCl_4, had already been prepared by Goddeffroy. The results of the work on the cæsium-mercury salts fulfil the expectations concerning the value of cæsium as a means of studying alkali double halides, for all the previously-discovered types have been made with this metal, and one type besides (Cs_2HgHl_5) that had not hitherto been discovered. B. H. B.

Some Double Halides of Silver and the Alkali Metals. By H. L. Wells and H. L. Wheeler (*Amer. J. Sci.* [3], **44**, 155—157).—During a systematic search for well-crystallised salts of the type M'X,AgX, three well-defined compounds of another type, 2M'X,AgX, were obtained. The author's experience indicates that these 2 to 1 compounds are more easily prepared and crystallise better than the 1 to 1 compounds. The salts described are 2CsCl,AgCl, 2RbI,AgI, and 2KI,AgI, of which the first two are believed to be new. Their preparation and properties, and the mode of analysis, are described, whilst crystallographical descriptions are furnished by S. L. Penfield. B. H. B.

Disruption of Silver Halides by Mechanical Force. By M. C. Lea (*Amer J. Sci.* [3], **43**, 527—531).—Some years ago the author found that a latent image, capable of development, could be produced on a photographic plate by the action of mechanical force, such as tracing lines with a glass rod. He has now investigated the behaviour of the haloïd salts of silver under high pressure and under shearing stress.

Silver chloride and bromide, precipitated with an excess of the corresponding acid, and silver iodide, precipitated with an excess of potassium iodide, were dried by exposure to air in the dark, wrapped in bright platinum foil, and exposed for 24 hours to a pressure of 100,000 lbs. per square inch, applied gradually by means of a screw. All three silver salts darkened to a deep greenish-black. The platinum foil was not attacked, and hence the author concludes that the halogens are not set free, but react with the small quantity of moisture present, with formation of halogen acid. The change cannot be due to rise of temperature, because the pressure was

applied very gradually, and the silver salt was wrapped in platinum foil, and the latter was placed between large pieces of metal.

In order to ascertain the effect of shearing stress, pure silver chloride was triturated in a porcelain mortar in presence of a solution of tannin or a solution of sodium carbonate; in both cases it soon darkened.

The air-dried chloride was also triturated alone in a chemically-clean mortar, and after about 15 minutes trituration was perceptibly darkened, the colour increasing in intensity as the process was continued. The product was violet-purple, and agreed in its properties with silver photochloride.

These results show that the molecules of haloïd silver salts can be broken up by mechanical forces in the absence of active light, and they establish the uniformity of the action of all kinds of energy on these salts (compare Abstr., 1891, 803). Any form of energy is not only capable of producing a latent image susceptible to development, as shown in previous papers, but can also bring about the actual disruption of the molecules. It would seem, therefore, that the phenomena of the latent image and its development are not exclusively, nor even especially, connected with light. The disruption of the molecules of the silver salts by mechanical force is the more remarkable in view of the fact that the decomposition of all three salts is endothermic. C. H. B.

Note by Abstractor.—The author claims that this is the first case of the mechanical decomposition of a compound formed by an exothermic reaction, but he seems to be unacquainted with Spring's experiments.

It is difficult to see how shearing stress (resulting from the sliding of one particle over another) was eliminated in those experiments where the air-dried salt was wrapped in platinum foil and compressed. C. H. B.

Formation and Properties of Tetracalcium Phosphate. By O. Foerster (*Zeit. angw. Chem.*, 1892, 13—22).—Tetracalcium phosphate may be produced by boiling ordinary calcium phosphate with very strong aqueous potash, part of the phosphoric acid being abstracted; or it may be produced by strongly heating calcium triphosphate with lime or calcium carbonate. If, however, tricalcium phosphate is fused with solid potassium hydroxide, the mass insoluble in water will consist of calcium hydroxide, which may be readily dissolved with sugar solution, some calcium carbonate, and undecomposed or, perhaps, regenerated tricalcium phosphate.

It has now been proved beyond doubt that basic slags principally consist of tetracalcium phosphate. Their superior value as a manure is due to the fact that the tetracalcium compound is more readily decomposed in the soil than the tricalcium compound. Like dilute mineral acids, the acids contained in the soil rapidly abstract not only the extra molecule of lime, but also another, leaving the readily soluble dicalcium compound. L. de K.

Dissociation of Barium Peroxide. By H. Le Chatelier (*Compt. rend.*, **115**, 654—656).—Anhydrous barium oxide, obtained by strongly heating barium carbonate with carbon, does not combine with pure and dry oxygen at 500°. If, however, the oxide is heated in a current of air saturated with aqueous vapour at 20°, absorption of oxygen takes place very rapidly, the product being a liquid which only solidifies at 450°. This mixture contains 66·6 per cent. of barium hydroxide and 33·3 per cent. of the peroxide.

Barium peroxide was finally prepared by heating the somewhat-hydrated peroxide at 700° in a current of pure and dry oxygen so long as any water was given off. The product is not quite pure, but contains the minimum quantity of water necessary to ensure absorption of oxygen.

The pressures observed for a mean degree of decomposition are as follows :—

Temperature...	525°	555°	650°	670°	720°	735°
Pressure.....	20	25	65	80	210	260 mm.

Temperature.....	750°	775°	785°	790°
Pressure.....	340	510	620	670 mm.

The pressures are higher at the commencement of the decomposition, and lower towards the end.

The decomposition of barium peroxide by heat is a complex phenomenon. The presence of water vapour is essential, and it would seem that a fused mixture of barium peroxide and barium hydroxide is an indispensable intermediate compound. The pressure that limits the dissociation has a theoretical value infinitely great when the peroxide is saturated with oxygen, and no barium monoxide is present in any form. As the decomposition proceeds, however, the pressure decreases until sufficient monoxide is formed to exist in the solid state. Beyond this point, the pressure remains constant so long as any peroxide remains in the solid state. As soon, however, as the peroxide no longer exists except in a state of solution in the fused mixture, the pressure gradually decreases, and becomes nil when decomposition is complete. The importance of the degree of decomposition compatible with the maintenance of a constant pressure is higher the less the quantity of water present, but the establishment of a condition of equilibrium takes place more and more slowly. The period of constant pressure disappears when the proportion of water reaches a certain limit, which, at 450°, is 10 per cent., the mass being then completely fused.

The pressure of the water vapour contained in the oxygen is without influence on the pressure of the oxygen itself so long as barium monoxide and peroxide are present. The fused mixture, so long as excess of its constituents is present, has a constant composition at each temperature, and consequently the pressure of the water vapour is constant in the same sense as that of the oxygen. If the presence of water vapour in the air used for the regeneration of the barium peroxide has not exactly the proper value, there will be absorption or elimination of water, with a consequent alteration in the proportion

of the fusible substances. If there is too little moisture, combination with oxygen becomes impossible; if there is too much, all the peroxide melts and becomes useless. C. H. B.

Phosphorescent Zinc Sulphide. By C. Henry (*Compt. rend.*, **115**, 505—507).—Phosphorescent zinc sulphide is obtained in large quantity by precipitating a neutral solution of pure zinc chloride with ammonia, redissolving the precipitate in excess of ammonia, and then exactly precipitating with hydrogen sulphide. The precipitate is carefully washed and dried, and is then heated almost to a white heat in a fire-clay crucible placed inside a plumbago crucible, brasqued with charcoal. The brilliancy of the phosphorescence seems to depend on the perfect purity of the zinc sulphide, and the product is either non-phosphorescent or feebly phosphorescent if zinc oxide or any zinc salt other than the chloride is used, or if alkali sulphides are used as the precipitant in place of hydrogen sulphide. Manganese sulphate, lead acetate, lithium carbonate, thallium carbonate, strontium chloride, basic bismuth nitrate, &c., all prevent phosphorescence.

The luminous intensity of the phosphorescence of the granular form of zinc sulphide, after excitation by the light from burning magnesium, is not less than 0·000215 of a candle-metre. The loss of light during the first 14 seconds is expressed by the formula $i_t = i_0 e^{-at}$ where i is the intensity of the light, and t is the time. The mean value of a, the velocity of emission, is 0·1970. The brightness of the sulphide in powder, when spread on a card, is represented by the equation $i^{0·5938}(t + 27·18) = 1647·5$; the results agreeing well with those of other observers. C. H. B.

Simultaneous Precipitation of Copper and Antimony by the Galvanic Current. By W. Hampe (*Chem. Zeit.*, **16**, 417—418).—The author, who regularly examines samples of electrolytic copper, has as yet always found a small quantity of antimony, varying from 0·007 to 0·02 per cent. Although antimony is supposed not to come down until the last portions of copper are precipitated, the author has found that it precipitates together with the copper from the beginning of the electrolytic operation.

The amount of antimony will be reduced to a minimum by often changing the acid copper solution. L. de K.

A Limited Reaction. By A. Colson (*Compt. rend.*, **115**, 657—659).—When 10 grams of mercuric chloride is boiled with 500 c.c. of benzene previously dried by distillation over phosphoric anhydride, it partly dissolves, and if dry hydrogen sulphide is passed into the liquid, hydrogen chloride is liberated, and, after 20 hours, if all trace of moisture has been excluded, the yellow chlorosulphide, $HgCl_2,2HgS$, is obtained. Similar phenomena are observed at the ordinary temperature. The limitation of the reaction is due to the formation of the molecular compound. It is not due to the retention of hydrogen chloride by the benzene, for if the chlorosulphide is introduced into the dry benzene along with fragments of sodium, it is practically unaltered even when treated with a current of hydrogen sulphide for

several hours. In presence of a trace of water, however, conversion of the mercuric salt into sulphide becomes complete.

Benzene solutions of mercuric salts react imperfectly with silicon sulphide, because the latter is insoluble in benzene. If, however, silicon sulphide is heated with mercuric chloride, silicon chloride is obtained together with mercuric sulphide; mercuric cyanide, under similar conditions, yields silicon cyanide as a yellow solid, soluble in water. C. H. B.

Probable Presence of Iron Carbonyl in certain Illuminating Gas. By GUNTZ (*Bull. Soc. Chim.* [3], **7**, 281—282).—The author noticed a deposit of ferric oxide on the cover glasses and porcelain reflectors of certain gas lamps which had been burning for some hours. He believes it to be due to the presence of iron carbonyl in the gas, this compound being probably formed by the interaction of the carbonic oxide contained in the gas and metallic iron which is used as a desulphurising agent. A. R. L.

Note.—The author makes no mention of the similar observations of Roscoe and Scudder, on the probable presence of iron carbonyl in water gas (Proc., 1891, 126), and of Thorne, as to its presence in coal gas which had been compressed in iron cylinders (*ibid.*).

A. R. L.

A Case of Solid Solutions. By E. A. SCHNEIDER (*Zeit. physikal Chem.*, **10**, 425—429).—When a solution of a sulphate containing a ferric salt is precipitated with barium chloride, a considerable quantity of iron is found in the barium sulphate in the form of ferric sulphate. The author finds that with varying quantities of barium sulphate and a constant quantity of iron, the volume of the solution being always the same, the relative quantity of iron in the precipitate is very nearly constant. With the same quantity of barium sulphate and varying quantities of iron, the amount of iron in the precipitate increases to a certain limiting proportion, and thereafter remains constant. The author considers that these results are very probably due to ferric sulphate being "dissolved" in the barium sulphate (compare Van't Hoff, Abstr., 1890, 1044). J. W.

Dissociation of Chrome Alum. By H. BAUBIGNY and E. PÉCHARD (*Compt. rend.*, **115**, 604—605).—A solution of chrome alum, even after repeated precipitation with alcohol, is always acid. 20 c.c. of a saturated solution, when treated with 0·03 gram of ammonia gas, is neutral to methyl-orange. After some time, the liquid deposits violet crystals, which have a distinctly acid reaction, whilst the mother liquor is also distinctly acid to methyl-orange. There is partial dissociation of the salt, and the condition of equilibrium is such that the liquid is acid. Chromium sulphate behaves in a similar manner, but ordinary alum and aluminium sulphate show no such behaviour, their solutions remaining neutral to methyl-orange for eight days.

C. H. B.

Atomic Weight of Palladium. By H. F. KELLER and E. F. SMITH (*Amer. Chem. J.*, **44**, 423—434).—The metal was electrolytically

precipitated from an aqueous ammoniacal solution of pure palladiodiammonium chloride (compare Abstr., 1890, 831), and a full account is given of the special precautions taken in preparing this salt, which was made from commercial palladium containing copper, platinum, iridium, gold, and iron. Two series of experiments were made, the first consisting of three estimations, giving 106·920, with an extreme difference of 0·013, the second consisting of six estimations, giving 106·911, with an extreme difference of 0·070. The value deduced from the two series was 106·914 (H = 1, N = 14·01, Cl = 35·37). Keiser's value, 106·35 (Abstr., 1890, 17), obtained by reducing palladiodiammonium chloride in hydrogen, is deemed to be erroneous, partly owing to the impurity of the salt, and partly to the volatilisation of the metal and mechanical loss of the salt on heating. A number of experiments are quoted in confirmation of this view. By converting the palladammonium chloride into palladium sulphide by heating it in hydrogen sulphide, a value 107·07 was obtained, which the authors regard as confirming their other results.

Jn. W.

Note.—Bailey and Lamb (Trans., 1892, 745) obtained 105·459 as the mean result of determinations by several methods.

Compound of Gold and Tin. By A. P. Laurie (*Phil. Mag.* [5], **33**, 94—99).—Matthiessen, from a study of the electric conductivity of alloys of gold and tin, concluded that there must exist three compounds of these metals with each other, for the conductivity curve showed three very sudden breaks, being shaped like a W. To these compounds he gave the formulæ Au_4Sn, AuSn, and Au_2Sn_3 respectively.

The author prepared a series of alloys of gold and tin, and investigated the electromotive force developed in a voltaic cell constituted as follows. In the inner cell a solution of gold chloride was contained, into which dipped a plate of pure gold. In the outer cell was a solution of stannic chloride, and into this a rod of the alloy was immersed. The results he obtained are exhibited in the following table:—

Percentage of tin in alloy.	E.M.F. in volts.
0	0·667
10·07	0·923
23·1	0·932
26·0	0·923
28·5	0·941
34·9	0·932
35·9	0·950
40·0	1·215
50·0	1·279
100·0	1·425

The values between 10 and 36 per cent. are constant., and evidently due to some definite compound of gold and tin, which determines the E.M.F. After 36 per cent. has been reached, the E.M.F. suddenly

rises; this would point to excess of tin being then present. The compound AuSn contains 37 per cent. of tin. No indication of Matthiessen's other compounds was obtained. J. W.

Mineralogical Chemistry.

Josephinite, a New Nickel-Iron. By W. H. MELVILLE (*Amer. J. Sci.* [3], **43**, 509—515).—Magnetic pebbles have been discovered in large quantities in the gravel of a stream in Josephine and Jackson counties, in Oregon, in the vicinity of the district in which the well-known nickel silicate has been found. The pebbles are irregular in shape, and their smooth surfaces are coloured greenish-black, interrupted by bright areas of the greyish-white alloy of nickel and iron. This metallic portion is of special interest, in that it was found on analysis to consist of 23·22 per cent. of iron and 60·45 per cent. of nickel. This composition corresponds with the formula Fe_2Ni_5. Evidence brought forward by the author points to the terrestrial origin of the pebbles described. For the new nickel-iron, the name of *josephinite* is proposed, in honour of the county in which it has been discovered. B. H. B.

Polybasite and Tennantite from Aspen, Colorado. By S. L. PENFIELD and S. H. PEARCE (*Amer. J. Sci.* [3], **44**, 15—18).—At the Mollie Gibson mine, one of the most productive mines in Colorado, the most abundant silver mineral is polybasite, which occurs massive with greyish-black colour and irregular fracture. This massive polybasite is not a pure mineral, as at first sight it appears to be. Some of the polybasite crystals are surrounded by a layer of siderite, then by a narrow zone of metallic mineral, and then again by siderite. As this seemed to be the nearest approach to the pure crystallised silver mineral, an analysis of it was made, with the following results:—

S.	As.	Sb.	Ag.	Cu.	Zn.	Pb.	$FeCO_3$.	$MnCO_3$.	Total.
17·42	6·10	0·26	49·51	12·92	2·45	10·58	0·46	0·13	99·83

These results do not agree with those obtained on analysing the massive mineral, but after deducting 12·81 per cent. of impurities in the analysis quoted, and 28·18 per cent. in the second analysis, both give ratios almost exactly those required by the formula $9Ag_2S\ As_2S_3$.

Along with the polybasite, patches of steel grey tennantite are met with. On analysis, this mineral yielded results corresponding with the formula $4Cu_2S,As_2S_3$. The sp. gr. of the mineral is 4·56.

B. H. B.

Plattnerite from Idaho. By W. S. YEATES and E. F. AYRES (*Amer. J. Sci.* [3], **43**, 407—412).—Plattnerite was regarded as a doubtful species until, in 1886, E. Kinch (Abstr., 1887, 451) described a well-authenticated specimen from Leadhills, Scotland. Since then

analyses of plattnerite, from Idaho, have been published by H. A. Wheeler (Abstr., 1890, 339), and by J. D. Hawkins (Abstr., 1890, 340). In the meantime, a considerable quantity of this material has been secured from a tunnel near Mullan, in Idaho. The plattnerite occurs in botryoidal nodules embedded in a mixed ochre of limonite and plattnerite. Its hardness is 5·5, and its sp. gr. 8·56. Analysis yielded:

Pb.	Ag.	Cu.	Fe,Al.	O.	Insoluble.	Total.
83·20	trace	0·14	1·20	12·93	0·82	98·29

Impurities being neglected, the mineral thus contains 86·55 per cent. of lead and 13·45 per cent. of oxygen. A crystallographical description of the mineral is given by E. F. Ayres. The crystals are tetragonal, and isomorphous with rutile (TiO_2), cassiterite (SnO_2), and polianite (MnO_2), minerals which have a similar composition.

B. H. B.

Penfieldite, a New Mineral Species. By F. A. Genth (*Amer. J. Sci.* [3], **44**, 260—261).—With minerals formed by the action of sea-water on ancient slags at Laurion, Greece, the author found a very few hexagonal crystals of a new mineral, for which he proposes the name of *penfieldite* in honour of S. L. Penfield. The crystals are white, and contain 18·55 per cent. of chlorine and 78·25 per cent. of lead. The formula is therefore $PbO,2PbCl_2$. B. H. B.

The Clinton Iron Ore. By C. H. Smyth, Jun. (*Amer. J. Sci.* [3], **43**, 487—496).—The author proposes to place the Clinton hæmatites in the category of original chemical deposits of date coeval with the enclosing strata. This result he bases on a careful study of this ore at the typical locality, Clinton, New York, his conclusion being that the oölitic ores at Clinton are not of secondary origin, but were deposited as hydrated ferric oxide in intimate connection with contemporary deposition of amorphous and chalcedonic silica. Hitherto the theory of pseudomorphous replacement of limestone has been generally accepted to explain the formation of the Clinton ore.

B. H. B.

Fluorine in Fossil Wood. By T. L. Phipson (*Compt. rend.*, **115**, 473—474).—Thirty years ago the author found, in the Isle of Wight, a specimen of fossil wood that contained 32·45 per cent. of phosphoric acid and 3·9 per cent. of fluorine. The wood was found in cretaceous grit, and seemed to have been fossilised by calcium phosphate and calcium fluoride. It had a brown colour and woody structure, and was sectile; sp. gr. = 2·17. C. H. B.

Herderite from Hebron, Maine. By H. L. Wells and S. L. Penfield (*Amer. J. Sci.* [3], **44**, 114—116).—The authors describe a new and interesting variety of herderite, almost free from fluorine. It consisted of a few yellowish-white crystals on albite, in form closely resembling those of childrenite. On analysis, it yielded the following results:—

P_2O_5.	FeO.	CaO.	H_2O.	F.	Insoluble.
40·81	15·32	32·54	5·83	0·40	5·27

The result confirms the idea advanced by Penfield and Harper, that fluorine and hydroxyl are mutually replaceable in herderite, and the formula deduced by them for the mineral is confirmed.

B. H. B.

Formation of Phosphate Nodules. By C. L. Reese (*Amer. J. Sci.* [3], **43**, 402—406).—It having been suggested that the South Carolina phosphates may have been formed by the action of swamp waters lying on beds of marl, the author has made a series of experiments to test the accuracy of this view. From his experiments, it certainly seems probable that both carbonic acid and the humus substances in fresh-water swamps play an important part in the accumulation and concentration of calcium phosphate. The marls, in the first place, contain a small percentage of phosphate, which would gradually be increased as the carbonate is removed. The changes taking place may be represented by the following equations:—

$$2CaCO_3 + H_4Ca(PO_4)_2 = Ca_3(PO_4)_2 + 2H_2O + 2CO_2.$$
$$2CaCO_3 + 2CO_2 + 2H_2O = 2H_2Ca(CO_3)_2.$$

The humus substances also give off carbonic anhydride on decomposition, and there is thus a further cause for concentration from this source.

B. H. B.

New Occurrence of Ptilolite. By W. Cross and L. G. Eakins (*Amer. J. Sci.* [3], **44**, 96—101).—In 1886, the authors described (Abstr., 1866, 990) the first occurrence of a new hydrous aluminium, calcium, and alkali silicate, to which they gave the name of ptilolite. They now describe a new occurrence of this mineral near Silver Cliff, Custer Co., Colorado.

On analysis, this mineral yielded

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
67·83	11·44	3·30	0·64	2·63	13·44	99·28

The empirical formula derived from this analysis is $R'Al_2Si_{10}O_{24} + 6\frac{2}{3}H_2O$, which is the same as that of mordenite, but, as Pirsson has already pointed out (Abstr., 1891, 276), the two minerals are physically unlike.

B. H. B.

Constitution of Ptilolite and Mordenite. By F. W. Clarke (*Amer. J. Sci.* [3], **44**, 101—102).—The data given by Cross and Eakins (see preceding abstract) lead to simple formulæ for the minerals under discussion. When it is recognised that part of the water in each mineral may be basic, the apparent anomalies disappear, and the compounds reduce at once to similar salts of the acid $H_2Si_2O_5$, an acid well known in the species petalite and milarite. Both ptilolite and mordenite become represented by the general formula $Al_2(Si_2O_5)_3R'_4 + nH_2O$; the only serious uncertainties being in respect to the hydration.

B. H. B.

Constitution of certain Micas and Chlorites. By F. W. CLARKE and E. A. SCHNEIDER (*Amer. J. Sci.* [3], **43**, 378—386).—The authors have received from the Curator of Minerals in the Imperial School of Mines in St. Petersburg, some highly important material bearing on their researches (Abstr., 1891, 529). These five specimens, on which the present paper is founded, are as follows:—(1) Waluewite, from the Ural; (2) clinochlore from the same locality, the Nikolai-Maximilian mine; (3) leuchtenbergite from Slatoust, Ural; (4) diallage serpentine from Syssert, Ural; and (5) white mica from Miask, Ural. From the analyses given of these minerals, the authors deduce the following empirical formulæ:—

Waluewite	$Al_{86}Mg_{76}H_{80}(SiO_4)_{78}O_{174}$.
Clinochlore	$Al_{38}Mg_{87}H_{143}(SiO_4)_{52}O_{113}$.
Leuchtenbergite	$Al_{42}Mg_{68}H_{143}(SiO_4)_{50}O_{121}$.
Serpentine	$Al_4Mg_{102}H_{136}(SiO_4)_{71}O_{35}$.
Mica	$Al_{75}K_{25}H_{46}(SiO_4)_{74}O_2F_5$.

The last of these minerals is evidently an ordinary muscovite. The others were examined in great detail by the authors. The clinochlore and leuchtenbergite are typical members of Tschermak's orthochlorite series (this vol., ii, 19); which, according to him, are mixtures of two end compounds, serpentine and amesite. How amesite behaves on ignition is not known; but serpentine splits up into olivine and enstatite. According to Tschermak's theory, a clinochlore of the composition SpAt should yield, on ignition, 18 per cent. of enstatite. Since no enstatite is actually formed, it is plain that the clinochlore and leuchtenbergite examined contain no serpentine molecules, and hence Tschermak's theory falls to the ground. The formation of spinel from the waluewite and the chlorites seems to follow a single quantitative law. If the spinel is deducted from the composition of each mineral, the soluble portion may be expressed as a mixture of olivine and magnesian garnet. That these minerals are actually formed is not proved; but it seems highly probable that the chlorites studied do split up, yielding water, spinel, garnet, and olivine as the final products of decomposition. B. H. B.

Quartz Boulder in Ohio Coal. By E. ORTON (*Amer. J. Sci.* [3], **44**, 62—63).—It is well known that boulders are occasionally met with in coal seams. In the United States, Ohio has furnished the largest number of cases. These have all been derived from a single coal seam, the Middle Kittanning seam. The author now describes a boulder recently discovered in the Sharon seam, the lowest of the series. It is noteworthy in that it is not a metamorphic sandstone or quartzite like those previously found, but is an excellent example of vein quartz, and it has not been worn by water or glacial action, but is as angular as if freshly broken from the parent mass.

B. H. B.

Augite and Plagioclase in a Minnesota Gabbro. By W. S. BAYLEY (*Amer. J. Sci.* [3], **43**, 515—520).—The author describes a fibrous growth around olivine, which resembles very strongly the

reaction rims that have been described as existing between olivine and plagioclase. A careful study of the phenomenon, however, disclosed the fact that the growth is not due to reactionary processes between the rock's constituents, but is simply an original intergrowth of two of them, it being, in fact, a granophyric aggregate of plagioclase and augite. The major portion of the latter mineral in the rock separated before the felspar, and fastened upon the surfaces of the already formed olivine and magnetite. In many cases, however, before the crystallisation of the augite had ceased, the felspar began to form, and the two minerals crystallised together.

B. H. B.

Mica-peridotite from Kentucky. By J. S. DILLER (*Amer. J. Sci.* [3], **44**, 286—289).—The author describes an eruptive rock from the Flanary Dyke, Crittenden Co., Kentucky. It is composed essentially of biotite, serpentine, and perofskite, with a smaller proportion of apatite, muscovite, magnetite, chlorite, calcite, and other secondary products. An analysis of the rock is given by the author, the results showing that, although belonging to the peridotites, this rock cannot be included in any of Rosenbusch's six types. Hitherto no peridotic rock has been recognised in which biotite is an original essential constituent, and the author, therefore, suggests for the Flanary Dyke rock the name of mica-peridotite. B. H. B.

Meteoric Iron from Hassi Iekna, Algeria. By S. MEUNIER (*Compt. rend.*, **115**, 531—533).—This meteorite, the fall of which was observed by some Arabs, is a mass of iron weighing 1250 grams. Its contours are rounded, and it is covered with a black crust of a uniform thickness of 0·5 mm. The interior is very coherent, and has in some parts a fibrous structure; a polished surface shows well-marked Widmannstattian figures when treated with hydrochloric acid. The mass consists essentially of a mixture of kamacite, $Fe_{14}Ni$, and plessite, $Fe_{10}Ni$, but contains lamellæ of schreibersite, and some pyrrhotine or troïlite; its sp. gr. is 7·67 at 14°, and its composition is Fe, 91·32; Ni, 5·88; Co, 0·81; Cu, traces; S, traces; insoluble residue, 1·04 = 99·05.

The Hassi Iekna meteorite belongs to the rare lithological type described by the author, in 1870, under the name of schwetzite.

C. H. B.

New Meteorite from Kentucky. By H. L. PRESTON (*Amer. J. Sci.* [3], **44**, 163—164).—In August, 1889, a meteorite was found in Kenton Co., Kentucky, interlocked in the roots of an ash tree 14 inches in diameter, at a depth of 3½ feet below the surface. It is a meteorite of the siderite variety, measuring 21 by 14 by 8 inches in its greatest diameters, and weighing 359½ lbs. It has numerous shallow pittings, and is entirely free from crust. On analysis, it gave the following results:—

Fe.	Ni.	Co.	Cu.	C.	S.	P.	Total.
91·59	7·65	0·84	trace	0·12	trace	trace	100·20

B. H. B.

Meteorite from Central Pennsylvania. By W. G. Owens (*Amer. J. Sci.* [3], **43**, 423—424).—This meteorite was found on September 25, 1891, upon the east side of Bald Eagle Mountain, Williamsport, Pennsylvania. It weighs 7 lbs. 1 oz., and resembles in general outline a human foot. It is pitted deeply, and is covered with a reddish-brown rust. Its sp. gr. is 7·06. When polished, and etched with dilute acid, the Widmannstätten lines appeared very distinctly. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	S.	Si.	Total.
91·36	7·56	0·70	0·09	0·06	trace	99·77

The meteorite could not have been of recent fall, as it was found covered with several feet of stones, and, as far as can be learned, it is the only specimen of the fall which has been found. B. H. B.

Meteorite from Indian Valley Township, Virginia. By G. F. Kunz and E. Weinschenk (*Amer. J. Sci.* [3], **43**, 424—425).—In the spring of 1891, a mass of meteoric iron was turned up by a plough in Indian Valley township, Floyd Co., Virginia. It weighs 31 lbs., and measures 11 by 8 by 5 inches. The surface is much corroded, and covered with a limonite crust. Analysis gave the following results:—

Fe.	Ni.	Co.	Cu.	P.	S.	Si.	Total.
93·59	5·56	0·53	trace	0·27	0·01	trace	99·96

The structure of this meteorite is very interesting, as it lies between the so-called breccia and hexahedral irons. Some parts of the mass exhibit a granular structure, identical with that of the Chattooga meteoritic iron. It is a question whether the granular structure is the original structure out of which hexahedral particles were formed through recrystallisation, or whether it is due to the fact that this iron, not being rich in nickel, has a lack of crystallising power.

B. H. B.

Meteorite from the Sierra de la Ternera, Chili. By G. F. Kunz and E. Weinschenk (*Amer. J. Sci.* [3], **43**, 425—426).—This meteorite was found in the Sierra de la Ternera, Province of Atacama, Chili. Although small, weighing but 650 grams, it is undoubtedly the entire meteorite, as the unbroken original crust shows. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Total.
83·02	16·22	1·63	0·00	100·87

This analysis places the iron near the Cape Iron group; but as the physical properties of this group of irons have been so little studied, it is impossible to say whether the structure coincides or not. The complete absence of phosphorus indicates that this meteorite is an exception to the rule, in not containing the characteristic phosphor-nickel iron. B. H. B.

Zinc-bearing Spring Waters from Missouri. By W. F. Hillebrand (*Amer. J. Sci.* [3], **43**, 418—422).—Zinc salts have been observed in inconsiderable quantities in certain springs in the south of France and New Zealand; but the spring waters described by the author are, it is thought, unique, in that their chief saline constituent is zinc sulphate. On the road from Joplin to Seneca, in Newton Co., Missouri, there is a series of springs varying in size, and discharging from ½ gallon to 3 gallons of water per minute. On analysis, the water from two of these springs was found to yield, respectively, 297·7 and 327·0 parts of zinc sulphate in 1,000,000. The source of the metallic salt constituents of these waters is, of course, to be sought in one of the deposits of zinc-blende so numerous in Missouri, although there is no known indication of zinc ores within a quarter of a mile of the springs. B. H. B.

Physiological Chemistry.

Respiration in Fishes. By C. Duncan and F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **17**, 165—181; see this vol., ii, 63).—The respiratory changes in fishes and other water-breathing animals was investigated in perch, trout, cray-fish, &c., by means of an apparatus modified from the ordinary forms of respiratory apparatus to suit the exigencies of the case. The apparatus is figured and fully described. In all cases, a control experiment with a mammal (rabbit) was carried on simultaneously.

The results, fully given in tabular form, come into three categories; in the first, there were from 3 to 4 c.c. oxygen per litre of water. A corresponding atmosphere, containing 8 to 11 per cent. of oxygen, was used for the rabbit; and both fish and rabbit got on well.

In the second group, the oxygen was reduced to 0·8—1·7 c.c. per litre, and the percentage for the rabbit to 2—4·5 per cent., in the air it was breathing. The rabbit and the fish both get dyspnœa, and, if left there long, die.

In the third set of experiments (0·7—0 c.c. oxygen for the fish), they soon turn over on their sides and die. W. D. H.

Dextrose in Blood. By M. Pickardt (*Zeit. physiol. Chem.*, **17**, 217—219).—The blood is best freed from proteïds and pigment by zinc acetate (Abeles, Abstr., 1891, 1399). It then is found to contain a substance which is fermentable with yeast, is dextrorotatory, and reduces Fehling's solution. The proof that this substance is dextrose is afforded by the phenylhydrazine test. W. D. H.

Fluorine in Bones and Teeth. By S. Gabriel (*Zeit. anal. Chem.*, **31**, 522—525).—The estimations made by Carnot (Abstr., 1892, 911) have given the following percentages of calcium fluoride in bones:—

Shaft of human shank bone.....	0·35 per cent.
Head of ditto	0·37 ,,
Leg bone of ox.....	0·45 ,,
Bone of sea-cow	0·63 ,,
Leg bone of elephant.....	0·47 ,,
Tooth of ditto.....	0·43 ,,
Tusk of ditto	0·20 ,,

The author, relying on the etching test, finds, indeed, traces of fluorine in the ash of ox teeth, but the indications are quite insignificant compared with those obtained from mixtures of bone ash with 0·2 per cent. of calcium fluoride, whence he concludes that the above, and all hitherto published numbers, are far too high. At the same time, his complete analyses always show a deficit of about 1 per cent., although several methods of analysis have been employed, and, as this deficiency cannot all be fluorine, he suggests the possibility of the presence of some element not hitherto observed. M. J. S.

The Relation of the Urinary Carbohydrates to Humous Substance. By E. Salkowski (*Zeit. physiol. Chem.*, **17**, 229—273).—The present article is largely polemical, and the author reaffirms his older view (with some new experiments), that the fatty acids (especially acetic) which are found in putrid urine originate from the carbohydrates of normal urine. These are two in number, dextrose and animal gum.

That the acids originate from humous substances, or that the humous substances originate from carbohydrates, is considered very doubtful; the humous substances in the urine increase on standing, but this appears to be independent of putrefaction. The amount of reducing substance is much greater than the humous substances will account for. The method adopted for the estimation of the carbohydrates is Baumann's method with benzoic chloride; Udranszky's method for estimating humous substances is used. Urine, freed from humous substances by long-continued heating with hydrochloric acid behaves like normal urine. W. D. H.

Alcaptonuria. By H. Embden (*Zeit. physiol. Chem.*, **17**, 182—192).—A case of alcaptonuria is recorded, in which the disorder had been present, apparently, throughout life, and in which other members of the same family suffered similarly.

Alcapton was described by earlier authors as catechol, or protocatechuic acid, by Kirk as uroleucic acid (trihydroxyphenylpropionic acid), and by Baumann and Wolkow (Abstr., 1891, 1128) as homogentisic acid. This substance probably originates from tyrosine, which, uniting with 5 atoms of oxygen, yields the acid in question, ammonia, carbonic anhydride, and water. How and when this unusual metabolic act occurs is to be the subject of further experiments. In the present case, homogentisic acid was the substance which occurred in the urine. W. D. H.

Poisoning by Hydrogen Sulphide. By USCHINSKY (*Zeit. physiol. Chem.*, **17**, 220—228).—The toxic action of hydrogen sulphide has been recently investigated by Pohl (*Arch. exper. Path. Pharm.*, **22**, 1) and Lehmann (*Arch. Hygiene*, **14**, 135). They state that sodium sulphide is formed, which causes death by paralysis of the nerve centres, especially of the brain. Lehmann states that œdema of the lungs is also produced. This was not, however, found in the present research, which was almost entirely directed to ascertaining whether the gas acts as a hypnotic, as Schulz states (*Münch. med. Woch.*, 1892, No. 16). No evidence that it acts as such was found, and, therefore, the view that sulphonal produces its effects by giving off hydrogen sulphide in the body is untenable. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

A New Bacillus in Rain Water. By A. B. GRIFFITHS (*Bull. Soc. Chim.* [3], **7**, 332—334).—The author has discovered in rain water, stored in an open barrel during a mild winter, a microbe which he names *Bacillus pluviatilis*. When cultivated on gelatin plates, it forms yellow colonies 2—10 mm. in diameter. It liquefies gelatin, and develops rapidly when grown upon a piece of potato, colouring it orange, and transforming the starch into glucose. The colouring matter is soluble in alcohol, benzene, chloroform, ether, and carbon bisulphide, but insoluble in water. The microbe is a true bacillus, and is not formed from spores; it has a length of 2—4 μ and a breadth of 0·6—0·8 μ, and is stained by aniline colours. It can only live in water containing organic matter; the cultures may be dried, but are killed by heating at 100° for 15 minutes. The bacillus does not appear to be pathogenic. When cultivated for several days on peptonised gelatine, a *ptomaïne*, $C_9H_{21}N_3O_5$, crystallising in white, clinorhombic, nacreous needles or prisms is formed; this compound has a slightly bitter taste and a neutral reaction, dissolves in 80 parts of water at 17°, and is very soluble in boiling water and in chloroform, fairly so in alcohol, but insoluble in ether. Its solutions give a white precipitate with sodium phosphomolybdate, a chestnut-coloured precipitate with Nessler's solution, and a yellow precipitate with tannin; its crystalline derivatives are the *hydrochloride*, the *platinochloride*, and the *aurochloride*. The ptomaïne appears to be non-toxic, but acts as a powerful diuretic. A. R. L.

Absorption of Atmospheric Nitrogen by Microbes. By BERTHELOT (*Compt. rend.*, **115**, 569—574).—With a view to throw some light on the mechanism by which the absorption and fixation of atmospheric nitrogen is effected by microbes, the author has made experiments with natural humic acid extracted from soils in which

absorption of atmospheric nitrogen was known to take place, and with artificial humic acid prepared from sugar. In each case, about 5 grams of humic acid was placed in a flask containing about 6 litres of air, and was mixed with some distilled water and 2 c.c. of water containing lower forms of vegetation which had developed in presence of light in a flask of ordinary water. The flasks were then very carefully stoppered, and exposed to diffused light for several months. In every instance white, microscopic, vegetable growths of many species developed, and a certain quantity of carbonic anhydride was formed. With natural humic acid, there was an increase in the combined nitrogen of 0·0104—0·0156 gram, or from 6 to 9 per cent., of the nitrogen originally present in the humic acid. With the artificial acid, there was a slight absorption of nitrogen.

In one experiment with natural humic acid, extending over about nine months, the quantity of nitrogen absorbed was 0·0545 gram, or 30·3 per cent., of the quantity originally present in the acid.

C. H. B.

Absorption of Atmospheric Nitrogen by Plants. By T. Schloesing, Junr., and E. Laurent (*Compt. rend.*, **115**, 659—661).—The experiments in which the direct absorption of atmospheric nitrogen has been established were made with soils comparatively poor in nitrogen. The authors have therefore repeated some of these experiments, using soils rich in nitric nitrogen. Under these conditions, the plants develop much more vigorously, but no fixation of atmospheric nitrogen was observed in the case of oats, colza, grasses, or potatoes.

C. H. B.

Carbohydrates of the Coffee Berry. By E. E. Ewell (*Amer. Chem. J.*, **14**, 473—476).—The portion of coffee insoluble in water contains, according to a communication made by Maxwell to the author, a substance which yields galactose under acid hydrolysis, and, according to Reiss (Abstr., 1889, 687), a substance which yields mannose under that treatment. The soluble portion contains cane sugar, to demonstrate the presence of which, the ground coffee, deprived of its fat by treatment with ether, is extracted with 70 per cent. alcohol. The extract is treated with lead acetate, the excess of lead removed by hydrogen sulphide, and the sugar precipitated as saccharate by the addition of strontium hydroxide to the boiling solution. The saccharate is then suspended in water, the base precipitated by carbonic anhydride, the water replaced by alcohol, and the sugar finally crystallised from the latter solvent. The process may be simplified with advantage by omitting the precipitation with strontium hydroxide. The percentage of saccharose, as estimated from the reducing power of the extract after treatment with lead acetate, removal of the excess of lead, and inversion, was 6·29.

The insoluble portion of coffee yields furfuraldehyde when distilled with dilute hydrochloric acid (sp. gr. 1·06), and therefore contains carbohydrates of the pentose group. An average of 0·22 gram, or 4·4 per cent., of the aldehyde, corresponding with 9 per cent. of pentose, was obtained from 5 grams of untreated coffee.

When coffee is extracted with 5 per cent. aqueous sodium hydroxide,

and the extract treated with alcohol (as in the separation of xylan from wood), a gum is precipitated, which, after washing in succession with alcoholic hydrogen chloride, alcohol, and ether, and drying over sulphuric acid, forms a greyish, translucent, hard, brittle, friable mass. On hydrolysis, this yields a reducing substance, equivalent to 74·2 per cent. of dextrose; furfuraldehyde (13 per cent.), on distillation with dilute hydrochloric acid; mucic acid (18·7 per cent.), on oxidation with nitric acid; and but a slight ash (0·84 per cent.) on incineration. It is thus probably a compound, the molecule of which contains one pentose and one galactose group (compare Lintner and Düll, *Zeit. angw. Chem.*, 1891, 538; Lippmann, Abstr., 1891, 284). The acid extract of coffee also yields furfuraldehyde and mucic acid.

Jn. W.

Relations between Fat-decomposing and Glucoside-decomposing Ferments. By W. Sigmund (*Monatsh.*, **13**, 567—577).—The author has extended his previous work (Abstr., 1890, 1455), and has examined the action both of glucoside-decomposing ferments and of oleaginous seeds, or the ferments contained in them, on glucosides. Emulsion and myrosin were chosen as representatives of the first class, and were found to have the power of hydrolysing olive oil to some extent. In the second series of experiments, amygdalin and salicin were mixed with either the triturated seeds of hemp, poppy, and rape, or emulsions prepared from them. That the glucosides had undergone hydrolysis under the influence of the ferments, was shown by the formation of hydrocyanic acid, benzaldehyde, and glucose from the amygdalin, and of saligenin and glucose from the salicin. This hydrolysis could not be induced by proteïd substances.

The author has further commenced an investigation of the hydrolysing power of the pancreas, and the results at present obtained appear to indicate that pancreatic juice is able to bring about the hydrolysis of the glucosides.

G. T. M.

An Acid from Beet Leaves. By E. O. v. Lippmann (*Ber.*, **25**, 3220).—The author has identified as hydrocaffeïc acid the acid which he formerly found (Abstr., 1888, 262) to be present in traces in the autumn in the leaves of the beet.

L. T. T.

Nitrogenous Constituents of the Seedlings of Vicia sativa. By E. Schulze (*Zeit. physiol. Chem.*, **17**, 193—216).—The following nitrogenous bases were found:—Asparagine, glutamine, leucine, amidovaleric acid, phenylalanine, traces of tyrosine, besides guanidine, choline, and betaïne. The first six probably originate from proteïds; asparagine is the most abundant. Further experiments as to the origin of guanidine are necessary. Choline comes from lecithin, and betaïne is present in the ungerminated seeds. Vicine is present in the ungerminated seeds also, but it disappears as germination proceeds.

W. D. H.

Analytical Chemistry.

Estimation of Hydrogen and Barium Peroxides. By A. Baumann (*Zeit. angw. Chem.*, 1892, 116—117).—From 2 to 5 c.c. of the solution of hydrogen peroxide is mixed in the author's apparatus with 10 c.c. of a saturated solution of potassium ferricyanide and afterwards with 5 c.c. of aqueous potash or soda. 1 c.c. of liberated oxygen equals 1·51862 milligrams of H_2O_2. Barium peroxide is estimated as follows:—About 0·5 gram of the substance is introduced into the outer chamber of the generating vessel and dissolved in a small quantity of dilute hydrochloric acid (1 : 10), and then from 2 to 3 grams of potassium ferricyanide is added. The inner glass cylinder is next filled with 10 c.c. of strong aqueous soda (1 : 2), and after cooling for some time, the liquids are mixed and the volume of oxygen is read off. 1 c.c. of this gas equals 7·5564 milligrams of BaO_2. L. de K.

Estimation of Hydrochloric acid in the Contents of the Stomach. By A. Kossler (*Zeit. physiol. Chem.*, **17**, 91—116).—An examination of the various methods adopted for estimating hydrochloric acid in the stomach contents led to the following results:—

Hoffmann's method (*Centr. klin. Med.*, 1889, No. 46) consists in estimating polarimetrically the amount of inversion produced in a solution of cane sugar; this is proportional to the amount of hydrochloric acid and the strength of the sugar solution, the temperature and duration of the experiment being constant. Later (*Verhand. internat. Med. Congress, Berlin*, ii, Abth. **5**, 201), instead of the inversion of cane sugar, he adopted the hydrolysis of methyl acetate into methyl alcohol and acetic acid, the latter being estimated by titration. Both methods give very exact results when applied to the stomach contents; it does not, however, indicate how much of the hydrochloric acid is united to proteïd.

Winter's method (*Bull. Méd.*, 1889, No. 95; 1890, Nos. 8 and 54) consists in taking three quantities of the stomach contents; the first is treated with excess of soda, evaporated to dryness, ignited, and the amount of chlorine estimated by titration with silver nitrate; the second specimen is evaporated to dryness and kept at 100° for an hour, after which it is treated like the first. The difference gives the amount of free hydrochloric acid. The third portion is ignited immediately and then the chlorine estimated. The difference between estimations 2 and 3 gives the quantity of hydrochloric acid united to organic substances and to ammonia. The values obtained for the free acid and that united to organic substances are too high; the source of error is that in evaporating, and incinerating, hydrochloric acid is formed from acid phosphates and chlorides of the alkaline earths.

Braun's method also yields too high results, as in his titration he reckons as hydrochloric acid the acidity of acid phosphates.

Leo's method (*Centr. Med. Wiss.*, 1889, No. 26) consists in neutralising free acid with calcium carbonate; he states that the acid phosphates present are not decomposed. The loss of acidity gives the

measure of free acid present. Wagner (*Pflüger's Archiv*, **50**, 371) and others have criticised this method. It, however, gives fairly accurate results if organic acids are first removed by extraction with ether.

Sjöqvist's method (Abstr., 1889, 302) is, in the presence of phosphates, attended with loss of hydrochloric acid. W. D. H.

Gas-volumetric Estimation of Iodine and Acids. By A. Baumann (*Zeit. angw. Chem.*, 1892, 70—72).—The author, who is still engaged on the subject, has, some time ago, communicated an easy and accurate process for the gas-volumetric estimation of iodine and also of acids (Abstr., 1892, 103, 538). Attention is now called to the fact that the success of the operation depends on the celerity with which the liberated iodine is mixed with the alkaline solution of hydrogen peroxide. The latter substance should not be used in large excess and should be rendered alkaline with solution of potassium hydroxide (1 : 1) immediately before use, and must be cooled.

L. de K.

Estimation of Nitric acid by its Specific Gravity. By G. Lunge and L. Marchlewski (*Zeit. angw. Chem.*, 1892, 10—12, 330—331).—See this vol., ii, 66.

Estimation of Nitrogen in Sodium Nitrate. By Alberti and Hempel (*Zeit. angw. Chem.*, 1892, 101—104).—As commercial sodium nitrate often contains a considerable percentage of potassium nitrate, the author would like to abolish the present conventional process of estimating the moisture and the impurities and taking the nitrate by difference or refraction.

The direct estimation of the nitrogen in Chili saltpetre is most conveniently effected according to the process communicated by Ulsch (Abstr., 1892, 1518), or by Lunge's nitrometer. L. de K.

Estimation of Nitrites. By J. Grossmann (*Chem. Zeit.*, **16**, 818—819).—The author proposes the following simple process, which is based on the fact that if dilute sulphuric acid is added to a boiling solution of a nitrite, the reaction takes place according to the equation $3NaNO_2 + H_2SO_4 = Na_2SO_4 + NaNO_3 + 2NO + H_2O$, and that, consequently, only two-thirds of the base is neutralised by the standard acid. To get correct results, the acid must not be standardised, as usual, with sodium carbonate, but with a pure nitrite. 3 grams of pure sodium nitrite is dissolved in a flask in 200 c.c. of hot water, and after adding 40 c.c. of normal sulphuric acid boiled, until all nitric oxide has been expelled, the excess of acid is then titrated with normal soda. The acid may now be used for the assay of any commercial nitrite, but as these generally contain some free alkali, this must be estimated in the cold and subsequently allowed for.

L. de K.

Estimation of Nitrogen in Nitrates and Nitro-compounds by Kjeldahl's Method. By L. Chenel (*Bull. Soc. Chim.* [3], **7**, 321—327).—The author finds that Jodlbaur's modification of Kjeldahl's method for the determination of nitrogen (Abstr., 1886, 834) gives values agreeing closely with the theoretical with certain inorganic nitrates, methylamine nitrate, nitroglycerol, and several

nitro-derivatives of benzene; whilst, in the case of the nitronaphthalenes, values corresponding only with 90 per cent. of the total nitrogen are obtained. The latter, however, gives good results, if the reduction is effected with phosphorus iodide instead of zinc dust. This is conveniently prepared by adding iodine (12 grams) to a solution of phosphorus (2 grams) in carbon bisulphide (15—20 c.c.), and evaporating to dryness on the water-bath. About 0·05 gram of the phosphorus iodide and 8 grams of water are added to a weighed quantity (0·5 gram) of the nitronaphthalene; concentrated sulphuric acid (25 c.c.) and mercury (0·7 gram) are introduced into the solution, and the remainder of the operation carried on as usual.

A. R. L.

Kjeldahl's Method of Estimating Nitrogen. By C. Arnold and K. Wedemeyer (*Zeit. anal. Chem.*, **31**, 525—533).—Various suggestions have been made for expediting the oxidation of organic substances during the heating with sulphuric acid. The simultaneous adoption of Gunning's proposal to add potassium sulphate (Abstr., 1889, 796) and that of Arnold to use both mercuric oxide and copper sulphate (Abstr., 1887, 78) not only shortens materially the time required, but renders the method applicable to many substances, such as the azo-compounds, those containing the pyridine group, &c., which, with other modifications of the process, fail to yield all their nitrogen as ammonia. The proportions recommended are:—0·5 gram of substance, 30—50 grams of sulphuric acid, 15—30 grams of potassium sulphate, 1 gram of mercuric oxide, and 1 gram of cupric sulphate. To moderate the frothing which results from the presence of potassium sulphate, only half the proposed quantity is added at first, and the remainder after 10—15 minutes boiling. No potassium sulphate is needed if 2—3 grams of zinc powder is added instead of the usual fragments of zinc.

To render the method applicable to both organic and inorganic nitrates, benzoic or salicylic acid should be dissolved in the sulphuric acid (3 grams in 40 c.c.) before this is poured upon the substance. After mixing well, the acid is heated to boiling, the mercuric oxide and cupric sulphate are introduced, and, after 10—15 minutes longer boiling, the potassium sulphate.

M. J. S.

Estimation of Phosphoric Acid in Basic Slag. By A. F. Jolles (*Zeit. anal. Chem*, **31**, 516—519).—For dissolving basic slag for analysis, two methods have principally been in use, that namely with sulphuric acid and that with hydrochloric acid. It is now, however, established that the calcium sulphate obtained when sulphuric acid is used encloses and protects particles of calcium phosphate. The method of H. and E. Albert consists in boiling the slag with hydrochloric acid until the liquid is reduced to a few cubic centimetres of a thick jelly of silicic acid, at which stage they state that the addition of water will leave all the silica undissolved. This statement the author cannot confirm. He recommends the following modification:—5 grams of the powdered slag is moistened with water in a basin, boiled with 40 c.c. of 30 per cent. hydrochloric acid, evaporated completely to dryness, heated in an air-bath at 120°,

moistened with hydrochloric acid, dissolved in water, filtered, and made up to 500 c.c. Of this, 50 c.c. is mixed with 15 c.c. of Joulie's citrate solution (400 grams of citric acid made up to a litre with ammonia of sp. gr. 0·9), and precipitated as usual with magnesia mixture. The results obtained agree closely with those given by the molybdate method. Albert's suggestion to dissolve the washed ammonio-magnesium precipitate and titrate with uranium solution leads to higher numbers, in consequence, seemingly, of the slow development of the end indication with ferrocyanide. M. J. S.

Estimation of Phosphorus by neutralising the "Yellow Precipitate" with Alkali. By C. E. MANBY (*Chem. Centr.*, 1892, ii, 267; from *J. anal. Chem.*, **6**, 82—85, 2).—In the analysis of steel and iron, the precipitate obtained with ammonium molybdate is dissolved in 15 per cent. ammonia and a little hot water, excess of ammonia is driven off by evaporation, 2 c.c. of nitric acid (sp. gr. 1·2) is added, the solution evaporated to dryness, and the residue ignited until all the ammonium nitrate has volatilised. The estimation is complete in 40 minutes. C. F. B.

Estimation of Sulphur in Slags. By J. TORREY (*Chem. Centr.*, 1892, ii, 265; from *J. anal. Chem.*, **6**, 86).—Very concordant results were obtained by Craig's method, the hydrogen sulphide being absorbed in permanganate solution. The sulphur in pyrites may be determined by igniting in a stream of oxygen and absorbing the sulphurous anhydride formed in permanganate, the residue being washed with hot water, and the wash-water added to the permanganate before the sulphuric acid is precipitated. In some cases, it is advisable to add a little magnesium chloride to the hydrochloric acid in which the slag is to be dissolved. C. F. B.

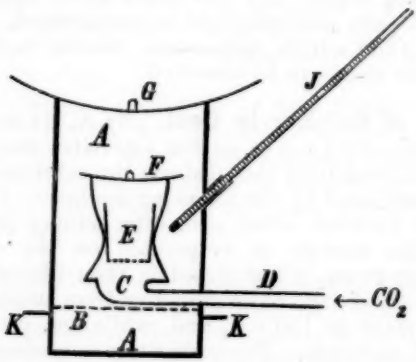
Estimation of Sulphur in Coal. By A. GRITTNER (*Zeit. angw. Chem.*, 1892, 170—171).—The author estimates the total sulphur by Eschka's process, and from this deducts the sulphur contained in the ash. This is estimated by the following method:—1 gram of ash is moistened with bromine water, and, after adding 100 c.c. of hydrochloric acid, the mixture is evaporated on the water-bath until reduced to about 10 c.c. The liquid is then filtered, the insoluble matter being washed until completely free from sulphates; the filtrate is next concentrated to 100 c.c., and, while hot, precipitated with a slight excess of ammonia. The precipitate is washed on a filter with boiling water until all sulphate reaction has ceased; the filtrate is acidified with hydrochloric acid, and the sulphate estimated as usual. The test analyses are satisfactory. L. DE K.

Volumetric Estimation of Sulphuric Acid in Alkali Sulphates. By C. CHERIX (*Chem. Zeit.*, **16**, 885).—The author proposes the following ingenious process:—Alkali sulphates are scarcely acted on by barium carbonate, but they are readily decomposed by barium hydroxide with formation of barium sulphate and caustic alkali. The unavoidable excess of barium is easily removed by a current of

carbonic anhydride, and the filtrate now contains alkali carbonate, which may be readily titrated in the usual manner by a standard acid and calculated into sulphuric acid. The presence of chlorides and nitrates does not in the least interfere. The two test analyses are very satisfactory. L. DE K.

Estimation of Arsenious Anhydride. By A. BAUMANN (*Zeit. angw. Chem.*, 1892, 117).—The process is based on the fact that an alkaline solution of potassium ferricyanide is rapidly reduced by arsenious acid, and will consequently evolve less oxygen when mixed with hydrogen peroxide. The difference in oxygen evolved, before and after the addition of the arsenious acid, serves as a measure of the latter. 1 c.c. of oxygen corresponds with 4·425 milligrams of arsenious oxide. L. DE K.

Estimation of Antimony and the Use of the Gooch Filter. By T. PAUL (*Zeit. anal. Chem.*, **31**, 537—543).—Antimony is most conveniently and accurately weighed in the form of trisulphide, but as the precipitate usually contains an excess of sulphur, either free or as pentasulphide, it requires to be heated in an atmosphere of carbonic anhydride. For this operation the Gooch crucible (see *Chem. News*, **31**, 181) presents several advantages. It allows the rapid filtration of large volumes of liquid, and the collection of either a large or small quantity of precipitate. For expelling the excess of sulphur, the author has constructed the apparatus here figured.



A is a cylindrical air bath with perforated false bottom *B*. *CD* is a glass tube, supporting the crucible *E*, and supplied with a stream of dry carbonic anhydride. *F* and *G* are glass covers through which the progress of the operation can be watched. Even when much sulphur is present, a temperature of 230°, maintained for an hour, suffices for its complete expulsion. M. J. S.

Estimation of Antimonious Oxide. By A. BAUMANN (*Zeit. angw. Chem.*, 1892, 117—118).—Antimonious chloride behaves

towards an alkaline solution of potassium ferricyanide like arsenious anhydride, and may be estimated in an analogous manner (see preceding page). 1 c.c. of oxygen equals 6·4573 milligrams of antimonious oxide. L. DE K.

Gas-volumetric Alkalimetry. By A. BAUMANN (*Zeit. angw. Chem.*, 1892, 114—116).—The process is based on the fact that a mixture of potassium ferricyanide and hydrogen peroxide does not evolve any oxygen unless free alkali is present. Very accurate results may be obtained, by using the author's apparatus, with the hydroxides of barium, calcium, potassium, and sodium, provided the two last are free from carbonic anhydride. The process is not suitable for taking the strength of ammonia. 1 c.c. of oxygen at N.T.P. = 5·0134 milligrams of potassium hydroxide, 3·5781 milligrams of sodium hydroxide, 6·0735 milligrams of barium hydroxide, and 3·30497 milligrams of calcium hydroxide. The solution of hydrogen peroxide should be perfectly free from acidity, and must, if necessary, be neutralised with calcium carbonate. L. DE K.

Estimation of Free Alkali in Commercial Hypochlorites. By N. G. BLATTNER (*Chem. Zeit.*, **16**, 885—886).—The author recommends one of the following three methods :—

1.—25 c.c. of the sample is mixed, in a 250 c.c. flask, with 50—100 c.c. of water, and then treated with an excess of ammonia, which decomposes the hypochlorite. The mixture is first gently heated, but is afterwards boiled down to a small bulk, so as to completely expel the excess of ammonia. After cooling, water is added to the mark, and the total alkalinity is now estimated in an aliquot part of the liquid by means of standard hydrochloric acid and methyl-orange. Another portion may be treated with solution of barium chloride, and the caustic alkali titrated with acid and phenolphthaleïn.

2.—10 c.c. of the sample is put into a 250 c.c. Erlenmeyer flask, and mixed with 150 c.c. of recently boiled, cold, distilled water and a few drops of a 1 per cent. alcoholic solution of phenolphthaleïn. If free alkali is present, the liquid will turn reddish, but on slowly adding standard acid, the colour will gradually disappear. The titration should be repeated, and it is as well to add another drop of phenolphthaleïn, when the reaction is finished, so as to make sure there is no more free alkali. The process, however, only gives the caustic alkali, whilst the first gives the alkali carbonate as well.

3.—Whilst engaged in investigating the action of metallic oxides on hypochlorites, the author thought of utilising the reaction between cobalt or nickel sesquioxide and a hypochlorite, by which the latter is reduced to chloride. Any free or carbonated alkali, may then be titrated with standard acid. To carry out the process, 25 c.c. of the sample is put into a 250 c.c. flask, diluted with water and first gently heated, but finally boiled, with a small quantity of precipitated cobalt or nickel sesquioxide. After cooling, water is added to the mark, and the alkali is estimated in the usual manner in 100 c.c. of the filtrate. L. DE K.

Detection of Strontium in presence of Calcium. By K. P. MacElroy and W. D. Bigelow (*Chem. Centr.*, 1892, ii, 424; from *J. Anal. Chem.*, **6**, 26).—The mixed carbonates of calcium and strontium are dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue extracted with a mixture of equal volumes of acetone and water. To the solution, a solution of potassium chromate in 50 per cent. acetone is added, when anhydrous strontium chromate is precipitated. If this is filtered off after 10 minutes, the filtrate contains no strontium, and only after several hours does calcium chromate crystallise out from it. C. F. B.

Qualitative Separation of the Barium Group. By A. Grittner (*Zeit. angw. Chem.*, 1892, 73—74).—The author, who has made a large number of careful experiments, has found that although barium may be readily detected by adding a solution of calcium sulphate, the test is not very delicate in presence of calcium and strontium compounds, especially when large quantities of the former are present. But even very minute quantities of barium may be detected in presence of calcium and strontium by adding to the acetic solution a solution of potassium or ammonium chromate, and he therefore recommends this method of separation. L. de K.

Schaffner's Volumetric Zinc Process. By E. Prost and V. Hassreidter (*Zeit. angw. Chem.*, 1892, 166—170).—This process, which is extensively used in France and Belgium, is briefly as follows:—2·5 grams of the zinc sulphide is treated with 12 c.c. of nitric acid, and then evaporated to dryness with excess of hydrochloric acid. The residue is moistened with 5 c.c. of hydrochloric acid, taken up with 50 c.c. of hot water, and treated with hydrogen sulphide. The precipitated sulphides are filtered off, and washed with a solution of hydrogen sulphide acidified with hydrochloric acid. The filtrate and washings are boiled to expel the hydrogen sulphide, and then again boiled with nitro-hydrochloric acid to oxidise any iron; after partial cooling, the liquid is introduced into a 500 c.c. flask, and mixed with 100 c.c. of ammonia and 10 c.c. of a saturated solution of ammonium carbonate. In the meantime, a standard zinc solution is prepared by dissolving about 1·5 grams of pure metallic zinc in a mixture of 20 c.c. of hydrochloric and 5 c.c. of nitric acid, and finally adding 300 c.c. of water, 100 c.c. of ammonia, and 10 c.c. of ammonium carbonate solution. After remaining over night, both liquids are made up to 500 c.c., and in 100 c.c. of the clear liquid, the zinc is estimated by means of sodium sulphide, using lead paper as indicator.

The authors have, however, found that the iron precipitate retains a not inconsiderable amount of zinc, and they therefore propose to add to the standard zinc solution approximately the same amount of ferric iron. Aluminium, if present, behaves like iron. Manganese must be got rid of by the addition of bromine water; hydrogen peroxide or sodium phosphate must not be used The precipitated manganic oxide is free from zinc. Lead (if not previously removed by hydrogen sulphide) and calcium are completely removed by the ammonium

carbonate, and their carbonates are free from zinc. It is of the utmost importance to render the whole of the silica insoluble.

L. DE K.

Volumetric Estimation of Thallium. By E. SPONHOLZ (*Zeit. anal. Chem.*, **31**, 519—520).—Thallious salts are instantly oxidised to thallic compounds by bromine water, 1 atom of thallium requiring exactly 2 atoms of bromine. A N/6 solution is of convenient strength. The exact strength must be ascertained by means of iodide and thiosulphate, and it is as well that this should be done with part of the contents of the burette which serves for the thallium titration, and as speedily as possible. The bromine is delivered into the acidified thallious solution from a burette whose jet dips into the solution, until an excess is indicated by the liquid becoming yellow. A correction is made for the amount of bromine required to colour the solution.

M. J. S.

Electrolytic Estimation of Copper. By G. P. DROSSBACH (*Chem. Zeit.*, **16**, 819).—Instead of using the usual acid solution, the author recommends electrolysing an ammoniacal solution of the copper. The precipitation proceeds more rapidly and the end reaction is more readily recognised; it also dispenses with the necessity of evaporating large quantities of free acid.

When using three middle-sized Meidinger cells, the author generally succeeded in finishing an analysis in about six hours. The current must, in every case, be stopped as soon as the last trace of copper has disappeared, otherwise other metals, such as nickel and zinc, may also come down. The process fails in presence of mercury and cadmium, and also of lead and silver, but these two are, of course, easily eliminated. Aluminium, arsenic, chromium, ferric iron, cobalt, nickel, zinc, tin, manganese, uranium, and bismuth do not sensibly interfere. The test analyses are remarkably accurate.

L. DE K.

Quantitative Analysis by Electrolysis. By F. RÜDORFF (*Zeit. angw. Chem.*, 1892, 3—7, 197—200).—The author uses by preference Meidinger's cells; if once properly filled and placed in a quiet spot, they keep in good working order for several months. As regards the strength of the current—8 cells give 2·6 c.c. of electrolytic gas per minute; 6 cells, 1·9 c.c.; 4 cells, 1·2 c.c.; 3 cells, 0·8 c.c.; and 2 cells, 0·02 c.c. of gas. The author's decomposition apparatus consists of a deep platinum dish, 60 mm. in height, 75 cm. in diameter, of about 40 grams in weight, and 170 c.c. capacity, and a stout platinum wire, one end of which is twisted like a spiral. Hemispherical dishes of 100—150 c.c. capacity answer the same purpose. As electrolytic precipitations take a rather long time, the author generally starts the analysis in the evening, when it will be completed early in the next morning. The author communicates what he considers to be improvements in the electrolytic separation of metals.

Copper.—The solution should not contain more than about 0·4 gram of the metal. Free acid should be neutralised with ammonia; 5 drops of nitric acid is then added, and the liquid made up to about 100 c.c. The electrolysis is effected by means of 2—6 cells, the basin being connected with the negative pole. When all the copper has

precipitated, the free nitric acid in the dish is rendered harmless by adding a little sodium acetate, the basin is disconnected, and the metallic copper washed, dried, and weighed. If the copper solution contains chlorides, the liquid is mixed with 3 grams of ammonium nitrate and 20 c.c. of ammonia, which, at the end of the operation, must be neutralised with acetic acid.

Mercury is estimated, like the copper, from an acid solution, or it may be precipitated from an ammoniacal solution after previously adding 0·5 gram of tartaric acid.

Silver.—The solution, which should contain about 0·3 gram of metal, is neutralised with sodium hydroxide and mixed with a slight excess of potassium cyanide. After diluting to about 100 c.c., the electrolysis is effected with the aid of 3—6 cells. The precipitated silver is thoroughly washed and dried at 100°.

Nickel.—The solution, which should contain about 0·3 gram of metal, is mixed with 25 c.c. of a saturated solution of ammonium sulphate and 25 c.c. of ammonia. After diluting to 100 c.c., the electrolysis is effected by means of 3—6 cells. Good results are also obtained by electrolysing an ammoniacal solution in presence of sodium pyrophosphate, using 4—6 cells. Chlorides should be absent.

Cobalt is estimated like nickel, using 6—8 cells.

Cadmium.—The solution, which should contain about 0·4 gram of metal, is, if necessary, neutralised, and mixed with excess of potassium cyanide. From 3 to 6 cells are used, and the precipitated metal is well washed with water, rinsed with alcohol, and dried at 80°, as at a higher temperature it is liable to oxidation.

Manganese.—The solution should, at most, contain 0·04 gram of manganese, which must be present as sulphate. After adding a few drops of dilute sulphuric acid and diluting to 100 c.c., the liquid is electrolysed by means of 2 cells. The manganese does not, however, separate as metal but as hydrated peroxide, which may be washed, dried at 60°, and weighed. Its weight multiplied by 0·523 equals the metallic manganese.

Zinc.—The solution, which should contain about 0·2 gram of metal, is mixed with 20 c.c. of a 25 per cent. solution of sodium acetate and 3 drops of acetic acid. 5—6 cells are used for the electrolysis, which is carried on in a platinum dish previously coated inside with metallic copper. The zinc solution should be free from nitrates or chlorides.

Iron.—The solution, which should contain about 0·3 gram of metal, is, if necessary, neutralised with ammonia and mixed with 60 c.c. of a saturated solution of ammonium oxalate. After diluting to 120 c.c., the metal is precipitated by means of 6—8 cells, and, after washing, dried at 100°, and weighed.

Lead.—The solution, which should contain about 0·1 gram of metal, is mixed with a few c.c. of nitric acid and 10 c.c. of a solution of copper nitrate containing 1 per cent. of metallic copper. The dish is connected with the positive pole and 3—4 cells are used, which cause the lead to precipitate, not as metal, but as peroxide, which may, after washing and drying at 120°, be weighed as such.

Tin.—The solution, which should not contain more than 0·3 gram of metal, is neutralised with ammonia and mixed with 30 c.c. of a

cold saturated solution of ammonium hydrogen oxalate. 3—6 cells are used, and the precipitated metal is finally dried at 80° and weighed. If the tin solution should be turbid, it must be cleared by gentle heating.

Bismuth.—The solution, which should contain not more than 0·1 gram of metal and but little free nitric acid, is mixed with but slight excess of strong solution of sodium pyrophosphate, then with 20 c.c. of a saturated solution of potassium oxalate and sulphate, and finally made up to 120 c.c. After exposing it to the action of 4 cells for about 20 hours, the precipitation of the bismuth will be found to be complete. After washing and drying at 60°, it may be weighed.

Antimony.—The solution, which should contain about 0·15 gram of metal, is mixed with 30 c.c. of a 10 per cent. solution of sodium monosulphide and electrolysed by means of 2—3 cells. The metal must be cautiously washed with water and dried at 60°. The author does not give any test analyses, but he invites analysts to try his processes and convince themselves of their usefulness. L. DE K.

Separation and Estimation of Tin, Antimony, Lead, and Copper in Alloys. By M. SCHMIDT and H. DREYER (*Chem. Zeit.*, **16**, 696).—About 1 gram of the finely-divided sample is fused in a porcelain crucible with 3 grams of dry sodium carbonate and 3 grams of sulphur for 20 minutes, to convert the metals into sulphides. The mass is extracted with water, and the insoluble matter collected and washed with a hot solution of sodium sulphide. The filter is then put into a beaker, heated with nitric acid to dissolve the sulphides of lead and copper, and the solution filtered and evaporated with sulphuric acid to separate the lead as sulphate. After washing this with dilute alcohol, the copper is precipitated by means of pure metallic zinc.

The alkaline filtrate is first acidified with hydrochloric acid and then heated on the water-bath with excess of the acid to redissolve the sulphides of antimony and tin. After filtering off from the sulphur, the liquid is heated for two or three hours with iron wire to precipitate the antimony. This is then washed with alcohol and weighed. As it may contain traces of copper, it must be treated with nitric acid and the copper estimated colorimetrically. The filtrate from the antimony, which now contains the tin, is diluted with water and treated with hydrogen sulphide. After the precipitate has completely subsided, it is collected, washed, and converted in the well-known manner into stannic oxide, which is then weighed.

The authors got very satisfactory results with this process, their analyses generally coming up to 99·7°. L. DE K.

Precipitation of Aluminium in presence of Lithium. By K. SPONHOLZ and E. SPONHOLZ (*Zeit. anal. Chem.*, **31**, 521—522).—The separation of lithium from aluminium by precipitation with ammonia from sulphate solutions is not complete with less than five precipitations. With ammonium acetate, one, or, at most, two, precipitations are sufficient. The dilute solution mixed with ammonium acetate is heated for a short time on the water-bath, adding during the heating

enough ammonia to keep the acidity low. The precipitate is transferred completely to a filter without suction, and is then washed by suction with hot water containing ammonium acetate until the spectroscope shows no lithium in the washings. It is immaterial whether the original solution contained sulphates or chlorides, and the presence of alkalis and alkaline earths does not affect the accuracy of the separation. M. J. S.

Estimation of Aluminium in Ferroaluminium. By E. Donath (*Zeit. angw. Chem.*, 1892, 13).—Regelsberger (this vol., ii, 48) has made use of potassium cyanide to prevent the precipitation of iron when throwing down the aluminium. The author claims to have investigated a similar process in 1880, and to have made use of sodium thiosulphate for the reduction of the ferric iron. Regelsberger's reducing agents, sodium hydrogen sulphite or iron wire, are less convenient, the former acting too slowly, and the latter unnecessarily increasing the amount of iron. The cyanide process may, however, be greatly improved by a preliminary precipitation of the alumina, care being taken that as little as possible of the iron is coprecipitated.

L. de K.

Analysis of Ferrochrome, Ferroaluminium, Ferrotungsten, Ferrosilicon, and Ferrotitanium. By A. Ziegler (*Zeit. anal. Chem.*, **31**, 558—563; from *Dingl. polyt. J.*, **279**, 163).—With the exception of ferrotitanium, these alloys are best attacked by fusing the finely powered substance with a mixture of 12 parts of alkali hydroxide and 6 parts of nitrate for half an hour in a silver crucible. To minimise the action on the crucible, it is advisable to heat with the small, smoky flame of a Bunsen's burner of which the air holes are nearly closed. The melt is boiled out with water; then, if chromium is present, the solution is treated for half an hour with carbonic anhydride, evaporated to dryness on the water-bath, redissolved, and filtered, washing with dilute sodium carbonate. In the filtrate, silica and chromium are estimated. The residue is dissolved from the filter with hydrochloric acid, and in the solution silica, manganese, and iron are estimated.

For estimation of the phosphorus, the fused mass is dissolved in nitric acid with a little hydrochloric acid, and then, by repeated evaporation with strong nitric acid, the hydrochloric acid is expelled before neutralising with ammonia and precipitating the phosphoric acid as usual.

Ferroaluminium requires a longer fusion than ferrochrome; the treatment of the solution with carbonic anhydride and the evaporation are in this case to be omitted. Another method is to dissolve the alloy in hydrochloric acid and evaporate the solution to dryness, adding nitric acid to oxidise the ferrous chloride, then transfer the residue to the silver crucible, and fuse with the mixture of alkali and nitrate.

Ferrosilicon may also be attacked by fusing with sodium hydrogen sulphate, if it is certain that no silicon hydride is formed. By avoiding a high temperature during the fusion, the metallic sulphates may be completely brought into solution when the fused mass is digested with hot water acidified with sulphuric acid.

Ferrotitanium can only be dissolved by fusion with sodium hydrogen sulphate and treatment with cold water. The filtrate from the silica is diluted to a litre, neutralised with ammonia, mixed with aqueous sulphurous acid, and boiled for two hours. The precipitate of impure metatitanic acid is fused again with bisulphate, and again precipitated as before, when a pure, white precipitate should be obtained. The filtrates should again be neutralised, reduced, and reboiled to ensure that precipitation has been complete.

In all cases the completeness of the attack and the purity of the precipitates must be confirmed. M. J. S.

Electrolytic Separation of Platinum and Palladium from Iridium. By E. F. Smith (*Amer. Chem. J.*, **14**, 435—437).—The combined influence of an alkali phosphate and phosphoric acid entirely prevents the electrolytic deposition of iridium from its solutions, but does not hinder that of palladium or platinum, so that either of the latter metals may be estimated by this means in the presence of the former. The metal is most conveniently deposited on a cathode consisting of a silver-plated platinum dish (see Abstr., 1890, 831). It is always bright and firmly adherent, and should be washed with hot water before being dried and weighed. If copper is substituted for the silver lining, a further washing with alcohol is necessary to avoid oxidation of the copper whilst drying; but this is objectionable, as the alcohol tends to loosen the deposit. The proportions to be observed, and the degree of accuracy to be expected, will be seen from the following trial experiments:—A solution (200 c.c.) containing palladium (0·1458 gram), iridium (0·1200 gram), hydrogen disodium phosphate (40 c.c. aqueous, sp. gr. 1·0358), and phosphoric acid (5 c.c. aqueous, sp. gr. 1·47) was subjected for a night to a current capable of liberating 2 c.c. of electrolytic gas per minute; the increase of weight of the silvered platinum dish was 0·1449 gram. Another solution (270 c.c.) containing platinum (0·1042 gram), iridium, phosphate, and phosphoric acid as before, was subjected for the same time to a current giving 1·8 c.c. of electrolytic gas per minute; the increase in weight of the dish was 0·1048 gram. Although the metal rhodium is completely deposited from its solutions under the above conditions, experiments made with the view of separating it from iridium did not prove satisfactory. Jn. W.

Estimation of Clay and Sand in Soils. By F. Tschaplowitz (*Zeit. anal. Chem.*, **31**, 487—501).—In the mechanical analysis of soils, it has been usual to regard as clay that portion which can be removed by elutriation under certain specified conditions. Calculated from the formula which, according to Schöne, connects the diameter, d, of a particle of clay with the velocity, v, with which it falls through water, $d = v\sqrt{}0{\cdot}0314$ mm., the upper limit of the diameter of the particles regarded as clay by Schlösing is 0·0005 mm.; by Mayer, 0·028 mm.; by Wolff and Knop, 0·01 mm.; by Orth and Laufer, 0·05 mm. The author's own experiments show that the majority of the particles in an ordinary clay have a diameter less than 0·006 mm., whilst those between 0·01 and 0·05 mm. are, at

least in some cases, nothing but crystalline sand. He therefore proposes that 0·01 mm. should be conventionally adopted as the superior limit, and recommends the following mode of procedure:—From 5 to 15 grams of the air-dried soil is boiled with 5 to 6 parts of water until all lumps are broken up. Sufficient 10 per cent. hydrochloric acid is then added to dissolve all carbonates, then more water and acid until the whole measures about 100 c.c. and contains 10 per cent. of free acid. It is again boiled and allowed to deposit for 24 hours. The turbid liquid is poured off and the sediment twice washed with warm water by decantation. The washed soil is next heated, but not boiled, with about 100 c.c. of 3 per cent. ammonia to dissolve humus, and washed as before. The turbid acid and alkaline washings are allowed to deposit completely, and the sediments from them are ignited and included in the clay result. The purified soil is next washed through a sieve of 0·1 mm. mesh, and the coarse particles are ignited and weighed. The liquid which has passed through the sieve is allowed to deposit for 24 hours or longer, the upper liquid is siphoned off, and if turbid is allowed further to settle. The purified soil is now submitted to the following process ("Aufschichtensmethode"):—A cylinder of 8 cm. diameter and 25 cm. (?) high is filled to a height of 20 cm. with distilled water. Upon the surface of this, by means of a funnel, the tube of which is bent at a right angle, the soil, suspended in 80—100 c.c. of water, is carefully delivered, 100 c.c. of water being further used for rinsing. After 20 minutes, the time required by Schöne's formula for particles larger than 0·01 mm. to subside, the liquid is drawn off by a siphon whose shorter leg is turned up for 2 cm. The residue is similarly treated as long as the water siphoned off is not clear. The portions of liquid siphoned off are warmed, and if they fail to settle clear they are evaporated to dryness, dried at 150°, or ignited and recorded as clay. The coarser sediment, together with that taken out by the sieve, constitutes the sand.

To determine the capacity of a soil for absorption of water, about 5 grams is weighed in a small, deep porcelain basin, with which a rounded glass rod has been tared. Water is then gradually added whilst the mixture is stirred to the utmost attainable uniformity. The stage of incipient fluidity, or that at which a furrow drawn with the rod begins instantly to fill up but does not disappear for a second or two, is easily determined to within three or four drops of water. It is well to overpass this stage, and then return to it by partially drying the paste and repeating the process. The weight of the water present is then ascertained. The absorptive power of a clay depends mainly on the average size of its particles, and is closely connected with its plasticity. M. J. S.

Gas-volumetric Estimation of Potassium Ferricyanide. By A. Baumann (*Zeit. angw. Chem.*, 1892, 113—114).—Potassium ferricyanide is readily tested as to its purity in the author's apparatus (compare Abstr., 1892, 103). The sample, dissolved in a small quantity of water, is introduced into the outer chamber of the generating vessel, and mixed with 5 c.c. of a solution of potassium hydroxide. From 5 to 10 c.c. of 2 per cent. hydrogen peroxide is put into the

annexed glass cylinder, and after the apparatus has been surrounded by cold water for some time, the operation is conducted as described in the former paper. 1 c.c. of liberated oxygen at N.T.P. corresponds with 0·029447 gram of potassium ferricyanide.

L. DE K.

Ammonium Magnesium Urate. By G. GUÉRIN and H. THORION (*J. Pharm.* [5], **26**, 202—204).—This salt, $(C_5H_2N_4O_3H)_{10}(NH_4)_8Mg + 4H_2O$, is easily obtained by precipitation. On adding magnesium solution to urine, the precipitate contains the whole of the uric acid as well as the phosphoric acid; hence the pyrophosphate resulting from ignition of the precipitate always contains an excess of magnesia, corresponding with the amount of uric acid present in the urine. J. T.

Estimation of a Mixture of Saccharose, Dextrose, and Levulose. By F. G. WIECHMANN (*Chem. News*, **66**, 237—239; 249—251).—The method to be described involves three analytical operations: two gravimetric determinations and one optical examination with the polariscope. Of course, the process is to be applied only in cases where no other optically active substance is present.

An amount of the sample equal to 10 grams of dry substance is weighed out, placed in an accurately graduated 100 c.c. flask, dissolved in water, and finally made up to the mark with distilled water.

Optical Examination.—Some of the solution is placed in a water-jacketed polarisation tube, provided with a thermometer, and a reading of the solution is taken in the polariscope at 20°. The reading thus obtained must be reduced to the basis of one made in a 100 mm.-tube, and, if a sugar scale has been used for the observation, the reading must be transformed into circular degrees. With a polariscope using 26·048 grams as the normal weight, the factor 0·346 is used for the sodium ray.

Gravimetric Estimation before Inversion.—10 c.c. of the solution (= 1 gram of dry substance) is made up to 150 c.c., and of this 24·4 c.c. (= 0·1628 gram of dry substance) is taken. 50 c.c. of Fehling solution is heated to boiling, the sugar solution is added and the mixture boiled for three minutes. After diluting the mixture with cold water, previously boiled, the cuprous oxide is collected on a weighed asbestos filter, and washed, first with boiling water, then with absolute alcohol, and finally with ether. The weighed precipitate is calculated to its equivalent of metallic copper, and from this figure the corresponding amount of saccharose can be ascertained. The total reducing sugars are calculated by adding 1/20 to the saccharose value indicated.

Gravimetric Estimation after Inversion.—50 c.c. (= 5 grams of dry substance) is heated on the water-bath with 4 c.c. of hydrochloric acid, sp. gr. 1·20, for five minutes at 67°. The flask is then removed, and after cooling to the original temperature, the contents are made up to exactly 100 c.c. Of this solution 20 c.c. is neutralised exactly with sodium carbonate, and made up to 150 c.c.; of this solution 24·4 c.c. (= 0·1628 gram of dry substance) is taken and treated with the alkaline copper solution as directed. The result expresses the total sugars as saccharose. If now the previously found saccharose value

is deducted, the difference will represent the actual amount of cane sugar.

As the specific rotatory powers of saccharose, dextrose, and levulose are accurately known, the operator will now be in possession of all the *data* required for an algebraic calculation of their percentages.

The test-analyses are highly satisfactory. The saccharose used in the experiments was made from the purest granulated sugar by repeated washing with absolute alcohol. The dextrose was prepared from commercial anhydrous dextrose by treatment with best blood carbon and repeated crystallisation from absolute alcohol. The levulose was prepared by inverting inulin with very dilute hydrochloric acid, and twice crystallising the product from absolute alcohol. It was then tested both optically and chemically, and found to be pure. L. DE K.

Estimation of Sugar in Cocoa Preparations. By M. SCHROEDER (*Zeit. angw. Chem.*, 1892, 173—183).—The author, who has conducted a large number of experiments, states that the detection and estimation of grape sugar in mixed cocoas or chocolates cannot be effected by Fehling's solution in the presence of cane sugar, as most commercial sugar contains a little invert sugar, which also gives reduction. Good results may, however, be obtained by using the polariscope as, when grape sugar is present, the rotation, after inversion, will be considerably less than it should be. By way of a check, the solution may be subjected to fermentation. Commercial grape sugar invariably contains amylin, which, not being fermentable, may afterwards be readily recognised both by optical and chemical tests. L. DE K.

Pentoses in Urine. By E. SALKOWSKI (*Chem. Centr.*, 1892, ii, 483; from *Centr. med. Wiss.*, 1892, 593—595).—Pentoses, possibly xylose, certainly occur at times in urine. To detect them, a little phloroglucinol is dissolved in warm hydrochloric acid, a slight excess of the former being taken; the solution is divided into two equal parts: to one, 0·5 c.c. of the urine to be examined is added, to the other an equal volume of normal urine of about the same concentration. The latter hardly changes in colour, but the former, if pentoses are present, becomes red at the surface, and the red colour gradually extends down into the liquid; this red colouring matter is dissolved on shaking with amyl alcohol. 0·5 per cent. of arabinose can be very easily detected by this method; 0·1 is recognised only with difficulty.

C. F. B.

Volumetric Estimation of Phenol in Urine. By A. KOSSLER and E. PENNY (*Zeit. physiol. Chem.*, **17**, 117—139).—The two volumetric methods of estimating phenol are those of Koppeschaar (*Zeit. anal. Chem.*, **15**, 233) and of Messinger and Vortmann (*Ber.*, **22**, 2313).

Koppeschaar's method consists in adding an excess of a mixture of alkali bromide and bromate (in the proportion of 5 mols. to 1), and acidifying with hydrochloric acid, when bromine is liberated; potassium iodide is then added, and the iodine set free is estimated with thiosulphate, the deficiency in the amount of the bromine liberated indicating the amount of phenol present.

Messinger and Vortmann dissolve 2—3 grams of phenol in soda, so that there are at least 3 mols. of soda to one of phenol. The solution is diluted to 250—500 c.c., warmed to 60°, and decinormal iodine solution added in excess. After cooling, dilute sulphuric acid is added, and the excess of iodine estimated with sodium thiosulphate. 6 atoms of the iodine, which has been used up, correspond with one of phenol.

Koppeschaar's method gives good results, but is not so accurate as Messinger and Vortmann's for small quantities of cresol. The latter method gives good results with both phenol and cresol. In estimating phenol, it is necessary in order that it may be wholly transformed into tri-iodophenol, that there should be present somewhat over 3 mols. of sodium hypoiodite to one of phenol, and that free iodine (5 c.c. of decinormal solution) should be present.

In estimating cresol, constant results are obtained if to each molecule more than seven of hypoiodite, and at least 15 c.c. of decinormal iodine solution, are present.

Applied to urine, these methods give higher results than the methods previously adopted. In the 24 hours urine, as much as 0·07, and in one case 0·106 gram of phenol was present. W. D. H.

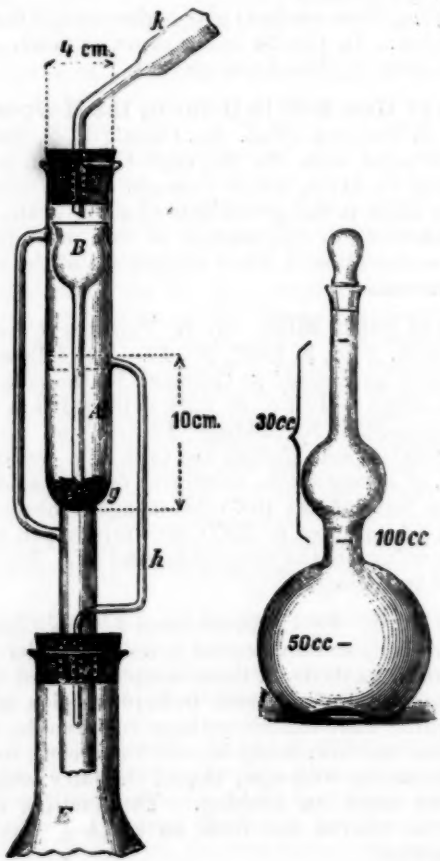
Estimation of Uric Acid in Urine by the Haycraft-Herrmann Method. By E. Deroide (*Bull. Soc. Chim.* [3], **7**, 363—364).—The high results obtained with the Haycraft-Herrmann method of estimating uric acid in urine, which depends on the volumetric determination of the silver in the precipitate of silver urate, are not due to the want of constancy in composition of this precipitate, but to the simultaneous precipitation of silver compounds of the xanthine group insoluble in ammonia. A. R. L.

Estimation of Fat in Milk. By W. Thörner (*Chem. Centr.*, 1892, ii, 429; from *Molk. Zeit.*, **2**, 1892, No. 1).—The following rapid and exact method is to be adopted in Germany by the police officials, and is described in detail:—10 c.c. of milk is placed in a tube of special shape, and saponified by adding 1·5 c.c. of alcoholic potash (16 grams per litre), and placing the tube in a water-bath for two minutes. 1 c.c. of strong acetic, sulphuric, or other acid is then added, to separate the fatty acids; the tube is again heated, then centrifugalised for 1—4 minutes at 2000 revolutions per minute, heated to 100°, and the volume of the fatty acids read off. For further details the paper must be consulted. C. F. B.

Analysis of Lard. By C. Amthor and J. Zink (*Zeit. anal. Chem.*, **31**, 534—537).—This communication gives the results of the examination, by recognised methods, of three samples of lard rendered in the laboratory from the fat of different individual pigs, and at different times of the year. They exhibit nothing remarkable, except that the iodine absorption was low, being 50—52·6 per cent. in the fresh lard and slightly decreasing with age; that of the fatty acids (51·6—52·27) diminished even more on keeping. The melting and solidifying points of the fat altered but little on keeping; those of the fatty acids rose somewhat.

In estimating the iodine absorption, it is immaterial whether a large or a small excess of iodine be added, but an old iodine solution gives more concordant results than a new one. M. J. S.

Analysis of Mixtures of Saponifiable and Unsaponifiable Fats. By M. Hönig and G. Spitz (*Zeit. angw. Chem.*, 1891, 565—568). —The two processes chiefly employed are very unsatisfactory, and have caused many complaints. An exception must, however, be made in favour of a method recommended by Morawsky and Dembsky, which consists in shaking out the soap solution with light petroleum. With care, this process gives not only concordant but also absolutely trustworthy results The authors, who have thoroughly investigated the process, now operate as follows:—7 to 10 grams of the sample is boiled in a reflux apparatus with 20—25 c.c. of alcoholic potash and the same volume of alcohol for about two minutes. 30—40 c.c. of



water is added, and the boiling repeated. After cooling, the soap solution is transferred to a separating funnel, and the flask rinsed, first with a little 50 per cent. alcohol, and then with 50 c.c. of light petroleum. The whole is now thoroughly shaken, and then allowed to remain at rest. The petroleum soon separates cleanly from the soap solution. The latter is drawn off, and the petroleum is washed a few times with 10 to 15 c.c. of weak alcohol, the washings being added to the main liquid. The soap solution must now again be shaken out with fresh petroleum until this, on evaporation on filter paper, yields no fatty residue. The petroleum washings, after being in turn washed with alcohol, are added to the main liquid, which is then distilled off. The residue, consisting of the unsaponifiable fat, is then weighed.

If a great many estimations have to be performed, the quickest way is to extract the soap solution in one operation, for which the authors have devised the following Soxhlet-like apparatus (see illustration). The soap solution, which should not exceed 50 c.c. in bulk, is put into the container *A*, in which has been previously introduced a layer of small glass beads, *g*, 1 cm. deep. The surface of the soap solution should reach up to about 5 mm. from the mouth of the drawing-off tube *h*. The funnel-shaped tube *B* (the upper part of a thistle funnel) is now put in its place, the apparatus connected with the extraction-flask *E*, and another 20 c.c. of light petroleum is added. The whole apparatus is then connected with a reflux condenser, and the petroleum is boiled until the soap solution seems quite clear, and the petroleum which runs off is quite colourless. As a little soap also dissolves, this must be removed by finally agitating the petroleum a few times with 50 per cent. alcohol.

If, for technical purposes, only an approximate estimation is required, the authors use a 100 c.c. flask (see figure), which also has a 50 c.c. mark. The neck is marked off in 30 c.c.

2 or 3 grams of the sample is put into the dry flask, and saponified with alcoholic potash. Alcohol is added up to the 50 c.c. mark, and then water up to the 100 c.c. mark. Light petroleum (boiling point 50—70°) is then added up to the top mark, and the whole is well shaken. After complete separation has taken place, an aliquot part of the top layer is pipetted off and evaporated, and the residual fatty matter is weighed. L. DE K.

Hübl's Iodine Numbers. By W. FAHRION (*Chem. Zeit.*, **16**, 862—863).—The author has finally adopted the following process:—About 0·15 gram of any fat or oil is dissolved in 10 c.c. of pure chloroform and mixed first with 10 c.c. of a 6 per cent. alcoholic solution of mercuric chloride, and then with 10 c.c. of a 5 per cent. alcoholic solution of iodine. After two hours, 20 c.c. of a 10 per cent. solution of potassium iodide is added. the liquid diluted to 150 c.c. with water, and then titrated with N/10 sodium thiosulphate, but without addition of starch. A blank experiment must, of course, be made, and, if the analysis is to be trusted, the check must take at least twice the amount of thiosulphate required by the fatty mixture. L. DE K.

Analysis of Mixtures of Ammonia and Methylamines. By H. QUANTIN (*Compt. rend.*, **115**, 561—562).—The impure methylamines are distilled with milk of lime, and the distillate is collected in pure water, which is then digested with sufficient freshly precipitated magnesium phosphate to convert all the bases, calculated as ammonia, into ammonium magnesium phosphate. The methylamine present maintains the necessary alkalinity, and the precipitation of the ammonia is practically complete, but if the liquid is poor in methylamine, a second treatment with magnesium phosphate may be necessary. The liquid when distilled yields the methylamines free from ammonia.

In order to make a quantitative analysis, the total alkalinity of the volatile bases is determined. The ammonia is then precipitated by sodium phosphate and magnesium sulphate in presence of methylamines, and the ammonia in the precipitate is estimated. The methylamines are converted into platinochlorides, and the trimethylamine salt is removed by washing with alcohol. The weight of the mixed platinochlorides of methylamine and dimethylamine, together with the weight of platinum left on ignition, enables the quantities of the two bases to be calculated. The trimethylamine is estimated from the total alkalinity by difference. C. H. B.

Estimation of Peptone by Precipitation as Mercury Peptonate. By L. A. HALLOPEAU (*Compt. rend.*, **115**, 356—358).—The neutral or very slightly acid solution of peptone, free from other proteïds, is mixed with its own volume of a solution of mercuric nitrate, and allowed to remain for 18 to 24 hours. The precipitate is then washed with cold water until free from excess of mercury, collected on a tared filter, and dried at 106—108°; the weight when multiplied by the coefficient 0·666 gives the weight of peptone.

The mercuric nitrate solution is prepared by heating 100 to 150 grams of pure commercial mercuric nitrate with a litre of water for 15 to 20 minutes. The liquid is filtered, heated nearly to boiling, mixed with sodium carbonate solution, drop by drop, with agitation, until a slight permanent precipitate is formed, again filtered, and diluted to one litre.

Chlorides, in the proportion in which they are present in commercial peptones or the gastric juices, do not affect the estimation, provided that a sufficient quantity of mercuric nitrate is added.

In order to remove other proteïds, the solution (supposed to be acid with hydrochloric acid) is exactly neutralised with sodium carbonate; syntonin is precipitated. The filtrate, faintly acidified with acetic acid, is heated on a water-bath for half an hour; albumin separates as a flocculent precipitate. The filtrate from the albumin is mixed with nitric acid drop by drop, until a permanent precipitate forms, and the liquid is agitated and allowed to remain until the hemialbumose separates. It is filtered off, and washed with a small quantity of water slightly acidified with nitric acid; the filtrate contains the peptone, and after being carefully neutralised with sodium carbonate, is treated in the manner described above.

C. H. B.

General and Physical Chemistry.

Rotatory Power of Salts of the Diamines. By A. Colson (*Compt. rend.*, **115**, 729—732; and C. Friedel, *ibid.*, 763—764).—Colson finds that when diacetyltartaric acid is saturated with ethylenediamine it yields a normal salt, which is very soluble in water but will not crystallise from it. A solution of 2·3 grams of the salt in 20 c.c. of water, in a column 200 mm. long, had a lævorotatory power of $-2°\ 56'$. The acid salt is soluble in water and crystallises in long prisms; a solution of the same strength as the normal salt, and under the same conditions, has a lævorotatory power of $-3°\ 55'$.

Normal ethylenediamine tartrate crystallises in lamellæ which are very soluble in water. 20 c.c. of an aqueous solution containing a quantity of salt equivalent to 1·2 grams of tartaric acid, in a column 200 mm. long, has a rotatory power of $+4°\ 54'$. A solution of only one-fourth the strength gave almost exactly one-fourth of the rotation, and hence it would seem that the dissociation of the salt by water takes place to a very slight extent. Ethylenediamine hydrogen tartrate is much less soluble in water, but the solution is distinctly dextrogyrate.

It will be seen that the rotatory power of all these salts is of the same sign as that of the acid from which they are derived. Most of them are exceptions to the rules laid down by Guye. Diacetyltartaric acid is lævorotatory, but its anhydride is dextrorotatory, and this difference is due, according to Guye and Le Bel, to the occurrence of a closed chain $(CO)_2O$, which alters the positions of the atoms H, C, C, H, but Colson finds that the normal salt of ethylenediamine, which also contains a closed chain, is lævogyrate, like the acid, and not dextrogyrate, like the anhydride. The hydrogen salt, according to Guye's views, should be dextrogyrate, but is, as a matter of fact, lævogyrate.

The author attaches great importance to what he terms the *conservation of the molecular type*. Whenever, without any profound alteration of its constitution, an optically active compound gives rise, directly, to a series of compounds, or inversely, it communicates to the latter its optical properties. All the tartrates are optically active, because they are derived from an active original, which they can regenerate, the dissymmetrical type of the tartaric acid being preserved in its derivatives.

In accordance with the same principle, an inactive acid cannot produce active salts, a conclusion which is, however, in contradiction to the theory of asymmetric carbon. This conception, which is unable to explain the formation of racemates, predicts, on the other hand, that certain citrates, tartronates, isosuccinates, glyceroxides, &c., possess optical activity, although glycerol, citric and tartronic acids, &c., are inactive.

Friedel points out that Colson attributes to Guye a statement which is quite contrary to the principles of stereochemistry, namely,

that in active tartaric acid the four atoms H, C, C, H are in the same plane. This might be the case in the inactive acid, but in the optically active acid, which according to the predictions of Pasteur, and also according to stereochemical theory, has no plane of symmetry, the four atoms are not in the same plane, much less in a plane of symmetry. Moreover, the plane which Colson regards as the plane of symmetry is not a plane of symmetry in inactive tartaric acid, but is perpendicular to the only plane of symmetry existing in a molecule built up from representative tetrahedra. C. H. B.

Rotatory Power of Salts of Diamines. By A. COLSON (*Compt. rend.*, **115**, 948—950).—A rejoinder to Friedel (preceding abstract).

Rotatory Power of Solutions. By G. WYROUBOFF (*Compt. rend.*, **115**, 832—834).—Solutions of strychnine have a lævorotatory power $[\alpha]_j = -132$, whilst solutions of strychnine sulphate have a rotatory power of only $[\alpha]_j = -30{\cdot}5°$. If this difference is due to the weighting of one side of the molecule by the sulphuric acid molecule, it follows that the rotatory power of strychnine selenate should be less. The rotatory powers of the two hydrates of strychnine selenate and strychnine sulphate, which are respectively isomorphous, are as follows:—

$(C_{21}H_{22}N_2O_2)_2,H_2SO_4 + 6H_2O$ ..... $[\alpha]_j = -27{\cdot}4°$
$(C_{21}H_{22}N_2O_2)_2,H_2SeO_4 + 6H_2O$ ..... $[\alpha]_j = -26{\cdot}9°$
$(C_{21}H_{22}N_2O_2)_2,H_2SO_4 + 5H_2O$ ..... $[\alpha]_j = -15{\cdot}6°$
$(C_{21}H_{22}N_2O_2)_2,H_2SeO_4 + 5H_2O$ ..... $[\alpha]_j = -17{\cdot}2°$

Similar relations are observed in the case of cinchonine:—

$(C_{19}H_{22}N_2O)_2,H_2SO_4 + EtOH$ ..... $[\alpha]_j = +185{\cdot}0°$
$(C_{19}H_{22}N_2O)_2,H_2SeO_4 + EtOH$..... $[\alpha]_j = +182{\cdot}5°$

the rotatory power of the cinchonine being +234°.

The rotatory power of anhydrous quinidine in solution in ethyl alcohol is $[\alpha]_j = +268{\cdot}6°$, whilst in methyl alcohol it is +257·5°. The difference is due to the fact that quinidine crystallises with one molecule of each of these alcohols, and the crystals are isomorphous.

$C_{20}H_{24}N_2O_2 + MeOH$..... $[\alpha]_j = +236{\cdot}1°$
$C_{20}H_{24}N_2O_2 + EtOH$..... $[\alpha]_j = +235{\cdot}3°$

Compounds geometrically and optically isomorphous have, in solution, specific rotatory powers which are practically identical.

The rotatory power of dissolved compounds, like the rotatory power of crystals, is a phenomenon of the nature of reticulation, which depends on the symmetry peculiar to the crystalline grating. Particles retain this symmetry in solution, and as the symmetry depends not only on the chemical molecule, but also on the water of crystallisation (or whatever is playing the same part), it follows that there is no dissociation in solution, much less a separation into ions.

C. H. B.

Transformation of Electrical into Chemical Energy. By L. MILLER (*Zeit. physikal. Chem.*, **10**, 459—466).—Gore (Abstr., 1892, 254), Regnauld, and others have maintained that there is a *sudden* change in the electromotive force of a galvanic element when the metal or alloy forming one of the electrodes passes through its fusing point. The author shows that this is theoretically impossible, leading to a contradiction of the second law of thermodynamics. He has also attacked the problem from the experimental side. A large test-tube was made to contain a galvanic element consisting of a suitable electrolyte and two metals, one of which could be fused below the highest temperature of experiment. The fusible metal was melted into the very short wide limb of a U-tube, the other limb being long and capillary. Contact was made by means of a platinum wire passing down the capillary tube. The bulb of the thermometer employed was dipped into the fused metal, which was then allowed to solidify. The difference of potential of the two metals was ascertained by means of a capillary electrometer, the error of experiment being about 0·001 volt. The temperature of the element was gradually raised, and the E.M.F. read off at every degree in the neighbourhood of the melting point of the metal. The combinations used were lead and silver in fused potassium and zinc chlorides, mercury and amalgamated cadmium in 50 per cent. sulphuric acid, and tin and silver in a fused mixture of the nitrates of potassium, sodium, and calcium. No sudden jump in the value of the E.M.F. was observed at the melting points of the lead, mercury, and tin. Accurate experiments with alloys are difficult to make on account of chemical changes at their surfaces. J. W.

The Clark Cell as a Standard of Electromotive Force. By R. T. GLAZEBROOK and S. SKINNER (*Proc. Roy. Soc.*, **51**, 60—67).—The authors have determined the absolute electromotive force of a Clark cell, prepared by Lord Rayleigh in 1883, in terms of a known resistance and the electrochemical equivalent of silver. The resistance (about 1 B.A. unit) was a strip of platinoid immersed in a bath of paraffin oil, and the current employed varied from 0·75 to 1·4 ampères. On the assumption that 1 B.A. unit is equal to 0·9866 ohm, that the quantity of silver deposited by 1 ampère in 1 second is 0·001118 gram, and that at the temperature coefficient of the E.M.F. is 0·00076, the E.M.F. of the cell at 15° was found to be 1·4342 volts, or 1·4324 volts at 62° F.

A large number of cells constructed at different times by Lord Rayleigh and others were examined, and very little difference was found between the electromotive forces, the variations from the standard being rarely greater than 0·0005 volt. Cells prepared in accordance with the provisional memorandum of the Electrical Standards Committee of the Board of Trade were also investigated with the same result.

Special experiments were made on the temperature coefficient of the E.M.F., the mean value obtained being 0·000755. When the temperature is rising, even although the rise be only a few degrees, the E.M.F. of the cell may lag considerably behind the temperature, especially if the cell be large.

The standard cells of the Board of Trade average 1·4339 volts at 15° C., or 1·4321 volts at 62° F. J. W.

Production of Hydrogen Peroxide in the Electrolysis of Aqueous Sulphuric acid. By V. KURILOFF (*J. Russ. Chem. Soc.*, **23**, 235—242).—The author has investigated the quantities of hydrogen peroxide and of persulphuric acid formed on the electrolysis of sulphuric acid solutions of different strengths. The apparatus he employed permitted the separate analysis of the liquids at the two electrodes. The hydrogen peroxide was determined by titration with potassium permanganate, and the persulphuric acid by adding a known quantity of ferrous salt to the solution and titrating back with potassium permanganate. His results are as follows:—

1. The quantity of hydrogen peroxide formed is very small.

2. Hydrogen peroxide and persulphuric acid may be formed simultaneously at both electrodes, but the peroxide is not always accompanied by persulphuric acid.

3. The formation of both products is intimately connected with the concentration. Persulphuric acid only appears when the solution contains over 10 per cent. of sulphuric acid; hydrogen peroxide when the concentration is greater than 1 per cent.

4. Mixtures containing 3, 47, and 73 per cent. of acid respectively behave differently from other mixtures with regard to the amount of hydrogen peroxide formed when they are electrolysed. This the author considers to be due to the approximation of their composition to that required by the hydrates $H_2SO_4,150H_2O$, $H_2SO_4,6H_2O$, and $H_2SO_4,2H_2O$, which are all said by Mendeléeff to exist in solution. J. W.

Heat of Combustion of Camphor. By BERTHELOT (*Compt. rend.*, **115**, 762—763).—Determinations of the heat of combustion of dextrogyrate camphor, by three different observers by means of the calorimetric bomb, gave as the mean results for the molecular heat of combustion +1414·2 Cal., +1413·5 Cal., and +1413·3 Cal. The general mean is +1413·7 Cal.

It follows that the heat of combustion of dextrogyrate camphor is practically identical with that of the lævogyrate and inactive forms, and is not 10 Cal. lower, as would appear from Louguinine's results. C. H. B.

Heat of Hydration of Maleïc Anhydride. By S. TANATAR (*J. Russ. Chem. Soc.*, **23**, 252—253).—Ossipoff (*J. Russ. Chem. Soc.*, **22**, 320) calculated the heat of hydration of maleïc anhydride from the heat of solution in excess of potash, and from the heat of solution of fumaric acid in the same solvent. The author points out that this is unjustifiable, since the final states of the two systems are not the same. J. W.

Thermochemical Data of some Organic Acids. By S. TANATAR (*J. Russ. Chem. Soc.*, **23**, 243—252).—

Levulinic Acid.

Heat of solution of solid acid, $C_5H_8O_3$	− 3·591 Cal.
Heat of neutralisation by KOH	+13·137 „
„ „ by NaOH	+13·267 „
Heat of solution in potash solution	+ 9·154 „
„ „ soda solution	+ 9·920 „
Heat of solution of $KC_5H_7O_3$	+ 1·440 „
„ „ $NaC_5H_7O_3$	+ 1·355 „
„ „ liquid $C_5H_8O_3$	− 1·393 „

Pyrotartaric Acid.

Heat of solution of $C_5H_8O_4$		− 4·894 „
Heat of neutralisation with KOH	1st equiv.	+13·579 „
	2nd „	+13·428 „
	total	+26·860 „
Heat of solution of acid in potash solution		+22·336 „
„ „ of $K_2C_5H_6O_4$		+ 6·089 „

Racemic Acid.

Heat of solution of $C_4H_6O_6$		− 5·803 „
Heat of neutralisation by KOH	1st equiv.	+12·955 „
	2nd „	+12·802 „
	total	+25·735 „
Heat of solution of $K_2C_4H_4O_6 + 2H_2O$		−10·438 „
„ „ $K_2C_4H_4O_6 + \frac{1}{2}H_2O$		− 5·834 „
„ „ $K_2C_4H_4O_6$		− 3·794 „

J. W.

Theory of Diffusion. By O. Wiedeburg (*Zeit. physikal. Chem.*, **10**, 509—516).—The author replies to the objections against his experimental methods and modes of calculation raised by Arrhenius (Abstr., 1892, 1265). J. W.

Rise of Salt Solutions in Bibulous Paper. By E. Fischer and E. Schmidmer (*Annalen*, **272**, 156—169).—Schönbein's experiments have shown that when bibulous paper is dipped into an aqueous solution of a salt, the water rises more quickly than the salt, and that the relative height attained by the latter is different for different substances; it is possible therefore to recognise the presence of the several constituents of a solution by taking advantage of this difference in behaviour. The authors are of opinion that the separation referred to is brought about by the difference in the diffusibility of the dissolved substances, a view which is supported by the fact that in the case of two salts, the one with the greater diffusion velocity rises more rapidly in the bibulous paper; the diffusion phenomena of all solutions which moisten bibulous paper can, in fact, be studied in this way just as well as with the aid of membranes. The apparatus employed for the purpose consists of a glass tube, in which six cylindrical rolls of bibulous paper are placed end to end, so that they are in close contact with the walls of the tube and with one

another; the end of the tube is then dipped into the solution to be examined, and kept vertically in this position at the ordinary temperature until the 5th roll is thoroughly moistened, which is usually the case at the end of three to four days' time. The glass tube is then broken at the points where the rolls touch one another, the papers separately extracted with water, and the solutions examined.

Employing a solution of sodium chloride (10 grams) and barium chloride (10 grams) in 100 c.c. of water, the proportion of the former to the latter expressed in grams was found to be 1·022, 1·230, and 1·364 in the rolls 1, 3, and 5 respectively, showing that the more diffusible sodium salt rises more rapidly than the barium salt.

With a solution of crystalline ferrous ammonium sulphate (10 grams) in 100 c.c. of water, the proportion of iron to ammonia in the 4th roll was found to be 1 : 1·686 when the proportion in the double salt is taken as 1 : 1; with a cold saturated solution of the same salt, the proportion in the 4th roll was 1 : 1·004; and in the 5th, 1 : 0·993. Similar results were obtained with solutions of ferrous potassium sulphate and nickel potassium sulphate; the dilute solutions showed a considerable amount of dissociation, whereas in saturated solutions the dissociation was inappreciable.

Further experiments carried out in a similar manner showed that the double salts formed by mercuric chloride with the chlorides of sodium and lithium are decomposed by water, but not by alcohol; mercuric ammonium chloride, however, is not decomposed by either solvent.

The following double salts, $NaH(NH_4)PO_4 + 4H_2O$; $KCN,AgCN$; $KNaC_4H_4O_6 + 4H_2O$, do not undergo dissociation in aqueous solution; the compound of dextrose with sodium chloride, $2C_6H_{12}O_6 + NaCl$, on the other hand, is partially separated into its components.

From experiments with solutions of naphthalene picrate, and of methylindole picrate in acetone and in alcohol, it would seem that no decomposition takes place.

The diffusion phenomena of ferrous ammonium sulphate, of the compound $2C_6H_{12}O_6 + NaCl$, and of mercuric sodium chloride were also examined with the aid of Rüdorff's apparatus; it was found that although the separation of the components of the first two substances in a given time is more effectively accomplished with the aid of membranes than with bibulous paper, the contrary is true in the case of the mercuric sodium chloride. F. S. K.

The Cryoscopic Behaviour of Weak Solutions. Parts V, VI, and VII. By S. U. Pickering (*Ber.*, **25**, 2012—2017, 2518—2524, and 3434—3440).—*Part V. Naphthalene and alcohol in benzene.*—These two series of results were examined in the same way as in the other cases previously described (Abstr., 1892, 678, 1045). With naphthalene, the results showed two breaks; with alcohol, one; the latter results have been examined by the mathematical, as well as the graphic, method (*Phil. Mag.* [5], **33**, 448), both methods leading to the same conclusion. The molecular depression in this case increases very rapidly with the dilution. *Part VI. Various substances in water*

and benzene.—In this part, the experimental details are given of determinations of which a summary has already appeared (Abstr., 1891, 971). *Part VII. General discussion of the results.* (For Parts I—IV, see Abstr., 1892, 678 and 1045).—In no case do the results obtained agree within experimental error throughout any appreciable range of strength with the values calculated according to Van't Hoff's formula corrected for supposed dissociation, nor can a single simple curve represent them without representing the error to be far larger than it is known to be. The representations of them as discontinuous curves with breaks, the positions of which were determined before the magnitude of the experimental error was known, have in every case been found to agree perfectly with this error, now that a method of determining it accurately has been obtained. The average difference (11 cases) between the apparent error of the points according to these drawings and the experimental error is only 0·4 per cent. The author quotes several instances to show that the splitting up of the figures into segments is due to the nature of the figure, and not to the method used in drawing them, and he tabulates the results, so as to show that the breaks cannot be attributed to imperfections in the thermometers used. Some evidence is also found in favour of these breaks indicating the presence of hydrates from the fact that there is a tendency for the same molecular proportions to recur in different cases; thus out of the 16 highest hydrates indicated there is one group of four in which the water molecules present are practically identical, two groups of three each, and two groups of two each; it is possible also that there may be a simple numerical relationship between the water molecules in higher and lower hydrates.

S. U. P.

Melting Points of Solvents as the Inferior Limit of Solubilities. By A. Etard (*Compt. rend.*, **115**, 950—953).—The solubility of naphthalene in hexane varies from 0·3 per cent. at −50°, the lower limit, to 78·8 at 70°; of triphenylmethane, from 1·2 per cent. at −30° to 97·1 per cent. at 90°; of diphenylamine, from 0·5 per cent. at −30° to 94·5 per cent. at 50°. That of naphthalene in carbon bisulphide varies from 1·2 per cent. at −60° to 90·3 at 70°; of triphenylmethane, from 3·4 at −60° to 92·2 at 80°; of diphenylamine, from 1·3 at −60° to 76·0 at 30°; of phthalic anhydride, from 0·03° at −40° to 30 2 at 180°. That of naphthalene in chloroform varies from 6·6 at −40° to 87·2 at 70°; of triphenylmethane, from 10·5 at −50° to 88·7 at 80°. The lines of solubility, which are in every case curved, are to be regarded as the loci of the melting points of mixtures of the solvent and dissolved substance.

Jn. W.

Cailletet and Colardeau's Method of determining Critical Points. By G. P. Grimaldi (*Real. Accad. Linc.*, 1892, i, 79—86).—The author criticises Cailletet and Colardeau's method of determining the critical temperature of liquids (Abstr., 1891, 779). By applying the method to the isothermals obtained by Amagat for carbonic anhydride, it is shown that the critical temperature lies between 28° and 35°. Further, an examination of the results obtained by Cailletet and Colardeau leads to the conclusion that the critical temperature of

water is only determined by their method within $\pm 5°$. The accuracy which Hinrichs (Abstr., 1892, 396) attributes to their determinations is hence impossible. W. J. P.

Effects of Gravity on Fluids at the Critical Point. By GOUY (*Compt rend.*, **115**, 720—722).—In all work with reference to the critical point, no attention has been paid up to the present to the compression of the fluid by its own weight, doubtless because the differences in the pressure produced in this manner appear inconsiderable when compared with the pressure of the fluid itself. But since at the critical point the compressibility is infinite, and very large in its neighbourhood, this is by no means the case. The author, selecting the case of carbonic anhydride, shows that the weight of the fluid exercises a very considerable influence on the results at the critical point. H. C.

Velocity of Sugar Inversion in presence of Acetic and Lactic acids. By A. SPERANSKY (*J. Russ. Chem. Soc.*, **23**, 147—150).—The following table contains the velocity constants of sugar inversion at 50° for solutions of lactic and acetic acids with or without the addition of salts. Equal volumes of the acid solution and of a 20 per cent. sugar solution were taken.

Solution.	Velocity constant.
Normal acetic acid	2·55
½-normal „	1·52
„ „ + ½-normal NaCl	2·67
Normal lactic acid	10·29
½-normal „	6·88
„ „ + ½-normal NaCl	10·02
„ „ + Na_2SO_4	4·40
„ „ + ½-normal sodium lactate	very small.

An equivalent quantity of barium chloride had nearly the same effect as sodium chloride.

The addition of sodium or barium chloride thus increases the velocity of reaction, whilst the addition of sodium sulphate diminishes it. J. W.

General Method of Chemical Synthesis. By R. PICTET (*Compt. rend.*, **115**, 708—712, and 814—817).—According to the theory which the author holds, all chemical action should be impossible at very low temperatures, and a series of very interesting experiments has been executed in order to show that this is the case. Aqueous sulphuric acid, containing 89 per cent. H_2SO_4 and solidifying at $-56°$, was brought when in the solid condition and at $-125°$ into intimate contact with finely powdered sodium hydroxide, also at $-125°$, and the two strongly compressed without any sign of chemical change occurring. The passage of electric sparks through the mass only causes action to take place in the path of the sparks, but this action is not communicated to the rest of the mixture. On warming, action suddenly commences at $-80°$, the heat evolved and

abrupt change of temperature causing breakage of the vessel containing the mixture. With sulphuric acid containing 35 per cent. H_2SO_4 and solidifying at −88°, similar results were obtained. Potassium hydroxide employed in place of sodium hydroxide remains in like manner unacted on below −90°. Concentrated ammonia and sulphuric acid do not act at all on one another below −80°; above this temperature, a limited action takes place under the action of electric sparks, and at −60—65° complete action suddenly occurs. Sulphuric acid and common salt do not react below −50°; from −50° to −25° there is limited action, and then complete action occurs. With the carbonates of calcium and sodium and 35 per cent. H_2SO_4, there is no action at −80°. The first bubbles of gas make their appearance at −56° with sodium carbonate, and at −52° with calcium carbonate, and the reaction becomes turbulent at −15° with calcium, and at −30° with sodium carbonate. All other carbonates behave similarly. With nitric acid in place of sulphuric acid, similar results were obtained in all the above cases, chemical action commencing, however, at a slightly lower temperature in each case. Metallic sodium, when brought into contact with aqueous alcohol, containing 84 per cent. alcohol, at −78°, undergoes no change. Action only commences at −48°, and then proceeds briskly. Sodium and 35 per cent. H_2SO_4 may be mixed at −85° without any action occurring, but, when heated up to −50°, a violent action suddenly commences, the hydrogen evolved inflaming spontaneously. Metallic potassium acts in a similar manner, but in this case change sets in at −68° instead of −50°. If sulphuric acid and an alcoholic solution of barium chloride are mixed at −85°, no change occurs, a precipitate first appearing when the solution is heated to −70°. At −40° the reaction is complete. Alcoholic silver nitrate and hydrochloric acid were mixed at −125° without reaction. At −90° action commenced, and was complete at −80°. Potassium hydroxide in alcoholic solution and phenolphthaleïn were mixed at −135° without any change occurring; a faint red tinge appeared at −100°, and the colour was pronounced at −80°. Litmus in contact with sulphuric and hydrochloric acids remains blue at −120°, a sudden change to red taking place in the one case at −105°, and in the other at −110°.

As general result of these observations, the author concludes that no action whatever takes place between the temperatures −125° and −155°, no matter what the nature of the reacting substances.

H. C.

Inorganic Chemistry.

Combustion of Hydrogen in Nitrous Oxide. By C. Montemartini (*Real. Accad. Linc.*, **7**, ii, 219—222).—The author finds that on passing mixtures of nitrous oxide with small quantities of hydrogen over palladium-black, the hydrogen is completely converted into water in accordance with the equation $H_2 + N_2O = N_2 + H_2O$.

The apparatus employed consists of a gas burette, containing the mixture of nitrous oxide and hydrogen, connected with a gas pipette by means of a glass tube containing palladium-black; both the tube and the burette are surrounded by water jackets, as an appreciable amount of heat is evolved in the condensation. The gas is passed four or five times over the palladium to ensure complete conversion of the hydrogen. The estimation of hydrogen by this method cannot be performed in presence of nitric oxide, owing to the absorption of the latter by palladium. It was found that 1 vol. of the metal at 18° absorbed 420·1 vols. of nitric oxide in two days with evolution of heat.

W. J. P.

Hydrogen Bromide. By E. Léger (*Compt. rend.*, **115**, 946—948).—A convenient method of preparing hydrogen bromide in quantity is to drop strong sulphuric acid from a tap-funnel on solid potassium bromide heated in a stoppered, tubulated retort on the water-bath. The gas given off is contaminated with small quantities of sulphurous anhydride and bromine, from which it is freed by two sets of wash-bottles, the first of which contains a strong solution of bromine in hydrobromic acid, the second, amorphous phosphorus suspended in hydrobromic acid. When all the sulphuric acid has been added, and the evolution of gas has slackened, the retort may be heated over a flame.

Another method is to pass sulphurous anhydride through a solution of bromine (1 vol.) in concentrated hydrobromic acid (1 vol.). The evolved hydrogen bromide is then purified as above. Jn. W.

Constitution of Hydroxylamine. By S. S. Kolotoff (*J. Russ. Chem. Soc.*, **23**, 3—5).—In view of the fact that hydroxyl compounds of nitrogen give up more or less readily the elements of water to form new nitrogen compounds, the author attempted to bring about the following reaction:—$NH_2{\cdot}OH + NH_3 = N_2H_4 + H_2O$. Experiment showed, however, that this reaction does not take place, even on heating at 100° for 24 hours. He is therefore of opinion that free hydroxylamine contains no hydroxyl, but is represented by the formula $H_2N{\cdot}O$.

When a salt of hydroxylamine is treated in Hentschel's nitrogen apparatus with bromine dissolved in excess of strong soda, only half of the nitrogen it contains is evolved in the free state, the other half being probably oxidised to acid. The reaction may be regarded as taking place according to the equation $2NH_3O = NH_3 + HNO + H_2O$, the ammonia being then oxidised. In order to test this view, the author oxidised in the cold a weighed quantity of a salt of hydroxylamine in a large excess of soda with the quantity of bromine calculated from the above equation. After the oxidation was completed, the excess of soda was neutralised with hydrochloric acid, and excess of copper sulphate added to the solution. The yellowish precipitate, which at once appeared, settled readily, and, after being collected and washed with water, was dried over sulphuric acid at the ordinary temperature, and weighed. The calculated quantity of $Cu(NO)_2$ obtainable, according to the equation from the amount of hydroxylamine salt taken, was 4·3 grams; the weight of the precipi-

tate was 4·9 grams, corresponding with the formula $Cu(NO)_2,H_2O$, which was confirmed by a determination of the copper in the precipitate. The copper salt does not lose weight at 136°, and blackens when treated with soda. The author considers it to be the dihydrogen cupric salt of "pyrohyponitrous acid," $H_4N_2O_3$.

Hydroxylamine sulphate loses weight at 125—130°, rapidly at 136°, 28·4 per cent. being the maximum loss. The ratio between the nitrogen and sulphur in the residue would appear to point to the formation of salts of N_2H_4 and N_2H_2. J. W.

Action of Sulphurous Anhydrde on Oxy-salts. By W. R. Hodgkinson and J. Young (*Chem. News*, **66**, 199).—The exposure of nitrates to a current of dry sulphurous anhydride results in their complete conversion into sulphates, with the evolution of nitrous fumes; the reaction is accompanied by a rapid rise in temperature, which occasions an explosion if the treatment is applied to gunpowder. Chlorates, by similar treatment, are also converted into sulphates, with the evolution of chlorine peroxide, which, at temperatures above 60°, decomposes with a flash and the production of sulphuric anhydride. Moist sulphurous anhydride acts more vigorously on chlorates than the dry gas; but, in most cases, without the visible liberation of chlorine peroxide. Dropping some alcoholic or ethereal solution of sulphurous anhydride on to powdered potassium chlorate causes the evolution of white fumes and a sharp explosion. The action of dry sulphurous anhydride on silver chromate results, apparently, in the formation of silver sulphate and chromic oxide; but with alkali chromates, dichromates, or permanganates, a partial conversion of the chromium or manganese into sulphate accompanies the formation of the alkali sulphate; the latter reaction goes on with rapidity at first. D. A. L.

Graphochemistry of Gunpowder. By E. Nickel (*Zeit. physikal. Chem.*, **10**, 454—458).—The author supposes gunpowder to consist of a mixture $mKNO_3 + nC + pS$, and on this basis finds graphically the limits between which the composition of a good powder must lie (compare Abstr., 1892, 1158). J. W.

Molecular Weights of Sodammonium and Potassammonium. By A. Joannis (*Compt. rend.*, **115**, 820—823).—Determinations of the vapour pressures of solutions of naphthalene in liquefied ammonia show that this liquid behaves as a normal solvent.

Measurements of the vapour pressures and of the boiling points of solutions of sodammonium and potassammonium in liquid ammonia show that the molecules of these compounds are represented by the formulæ $Na_2N_2H_6$ or $NaH_3N{\cdot}NH_3Na$ and $K_2N_2H_6$ or $KH_3N{\cdot}NH_3K$ respectively. C. H. B.

Silver Hemisulphate. By M. C. Lea (*Amer. J. Sci.* [3], **44**, 322—329).—Silver hemisulphate is obtained by the action of hypophosphorous acid and sulphuric acid on silver nitrate, phosphate, or carbonate; the last gives the best results, the action with the nitrate being too rapid, and that with the phosphate too slow. The most

convenient method is as follows:—40 grams of silver nitrate is precipitated with sodium carbonate, and the precipitate is well washed and mixed with a solution of 100 grams of sodium hypophosphite in 650 c.c. of water, to which 4 c.c. of sulphuric acid has been added. After a few minutes, a further quantity of sulphuric acid, 6 c.c., previously diluted with a little water, is added, and the mixture agitated until a bluish-black film of reduced silver begins to form on the surface, and at this point further reduction is prevented by neutralising the liquid with sodium carbonate. The reaction is usually complete in 20 to 25 minutes.

It is important that all the reagents should be free from halogens, and the solution of sodium hypophosphite before being acidified should be mixed with a small quantity of silver nitrate solution, allowed to remain, with occasional agitation, for several hours, and then filtered in order to remove the silver chloride.

The silver nitrate may be precipitated with sodium phosphate, but in this case about 24 hours is required for reduction.

The crude product is washed several times by decantation, and is then treated with nitric acid of sp. gr. 1·42 diluted with three times its volume of water, the quantity used being about twice the volume of the moist precipitate left after decanting the water. The acid is left in contact with the precipitate for three or four hours, and is then poured off, and the precipitate is well washed. After three successive treatments with acid in this way, the precipitate is very thoroughly washed with boiling water, and is then dried by exposure to air or at 100°.

The same product is obtained under a variety of conditions, and seems to be formed whenever a silver salt is brought into contact with a hypophosphite acidified with sulphuric acid. Hypophosphorous acid, however, has very little action on ready formed silver sulphate.

The colour of the silver hemisulphate thus obtained is bright brown, and is permanent when exposed to air, but changes to violet on heating for some time at 160°. No sulphuric acid is given off, even at a dull red heat. (In another part of the paper, the author states that the terra cotta or warm brown shade of the moist substance changes to pale lilac, by drying above 100°, becomes greyish at 165—170°, and yellowish-green at a higher temperature. Considerably below a red heat it acquires a fine ruby colour, which darkens almost to black during cooling, but then becomes paler, the cooled substance being pale olive-green.) Strong sulphuric acid is without action even at 100°; dilute nitric acid has very little effect, but the acid of sp. gr. 1·42 gradually dissolves the salt; ferrous sulphate is without action even after several days.

Alkali hydroxides slowly but completely convert the hemisulphate into a mixture of the hemioxide and the ordinary oxide, and the quantity of oxygen given off when this precipitate is strongly heated agrees with the constitution ascribed to the salt.

Hydrochloric and hydrobromic acids, and alkali chlorides and bromides, yield mixtures of the hemihalides and the ordinary halides, which spontaneously decompose into mixtures of the ordinary halides and metallic silver, the black colour of the hemihalide giving place

to the grey colour of metallic silver. The composition of the freshly obtained product agrees with the constitution ascribed to the hemisulphate.

The hemisulphate prepared in the manner described has the composition Ag, 76·44; O, 3·29; P_2O_5, 2·19; SO_3, 16·33; H_2O, 1·78 = 100·03, which agrees fairly well with the formula $7(Ag_4SO_4,Ag_2SO_4,H_2O) + Ag_6PO_4,Ag_3PO_4$. The quantity of phosphoric anhydride present is always about 2 per cent., and it cannot be removed even by treatment with hot strong sulphuric acid.

If the phosphoric acid is regarded simply as an impurity, the composition of the salt is $Ag_4SO_4,Ag_2SO_4 + H_2O$.

The author is of opinion that during the preparation of the salt the hemisulphate is produced in considerable excess, but is decomposed on treatment with nitric acid, the product being stable only when the ordinary salt and the hemi-salt are combined in molecular proportion.

Other hemi-salts of silver and oxy-acids probably exist, but they cannot be obtained by acting on the ordinary salts with hypophosphorous acid, although possibly they may be produced when the normal salts are formed in presence of sodium hypophosphite. The precipitate formed by adding silver nitrate to a solution of sodium citrate and sodium hypophosphite free from chlorides yields a rose-red solution when placed in a large quantity of water containing a small quantity of ammonia. C. H. B.

Fusion of Calcium Carbonate. By H. Le Chatelier (*Compt. rend.*, **115**, 817—820).—Chemically pure calcium carbonate in the form of an impalpable powder was enclosed in a steel cylinder and compressed between two steel pistons with a pressure of 1000 kilos. per square centimetre. A spiral of platinum wire embedded in the powder was heated by an electric current. Under these conditions, the calcium carbonate in the neighbourhood of the spiral can be fused without difficulty, there being a sharp line of demarcation between the part which has melted, and consequently become translucent, and that which has simply agglomerated under the pressure. A thin section of the fused portion shows minute crystals, and resembles certain specimens of marble that are but slightly macled.

The melting point of calcium carbonate under pressure approaches closely to the melting point of gold, but is not quite so high, a result which confirms the earlier observations of J. Hall. C. H. B.

Fusion of Calcium Carbonate. By A. Joannis (*Compt. rend.*, **115**, 934—936).—The fusion of calcium carbonate effected by Le Chatelier (preceding abstract) and Hall (*Journ. de Phys. de la Métherie*, **61**, 197, and **64**, 461), at a temperature between the melting points of silver and gold, and under a mechanical pressure of 300—1000 kilos. per sq. cm., was probably, to a large extent, the direct effect of the latter, in accordance with the well-known physical law. The author finds that neither the pure carbonate nor chalk melts when heated in a closed platinum vessel to a temperature even above the melting point of gold, although the pressure of the dis-

sociated carbonic anhydride may rise to 17 atmos. At the higher temperatures, the product, however, is crystalline, and resembles marble. Jn. W.

Zincoxides of the Alkaline Earths. By G. Bertrand (*Compt. rend.*, **115**, 939—941).—*Calcium zincoxide*, $Zn_2CaH_2O_3,4H_2O$, is obtained in brilliant, lozenge-shaped plates when ammonia is withdrawn from the ammoniacal solution of its proximate constituents. It absorbs carbonic anhydride rapidly from the air, becoming opaque, and is decomposed by water into zinc oxide and lime. It does not lose water at 125°, but is decomposed at a dull-red heat. *Strontium zincoxide*, $Zn_2SrH_2O_3 + 7H_2O$, made in a similar way, crystallises in flattened, lozenge-shaped plates. *Barium zincoxide*, $Zn_2BaH_2O_3 + 7H_2O$, crystallises in brilliant, flattened needles. These zincoxides may have the constitution $M''(O{\cdot}ZnOH)_2 + xAq$. Jn. W.

Action of Ammonia on Sulphates. By W. R. Hodgkinson and C. C. Trench (*Chem. News*, **66**, 223).—On heating silver, mercury, and bismuth sulphates to the melting point of zinc in a current of dry ammonia, they are entirely reduced; and, at a red heat, lead and thallium sulphates are completely decomposed, yielding a small quantity of the respective sulphides. Ferrous sulphate, anhydrous, crystalline, or as the double ammonium salt, is reduced, by the action of gaseous ammonia, to oxide containing 1 to 2 per cent. of sulphur; whilst the sulphates of zinc, magnesium, cobalt, nickel, manganese, and chromium, under similar circumstances, yield mixtures of oxide and sulphide in nearly molecular proportions. Copper sulphate, anhydrous or crystalline, absorbs ammonia, melts below 200°, turns black, appears to boil, and at about 400° decomposes with incandescence, leaving almost pure copper. The main volatile product is ammonium thionamate, and this, in a cooled receiver, where it comes in contact with the water, which is another product of the reaction, gives rise to ammonium sulphite; there is no ammonium sulphate, but probably a hydrazine compound is formed. D. A. L.

Double Salt of Lead and Potassium Iodides. By F. A. H. Schreinemakers (*Zeit. physikal. Chem.*, **10**, 467—476; compare Abstr., 1892, 560).—The double salt of lead and potassium iodides is not $PbI_2.2KI,2\frac{1}{2}H_2O$, as the author assumed from Ditte's analysis, but $PbI_2,KI,2H_2O$. The conclusions previously arrived at have, from this cause and from a more extended investigation, to be altered as follows:—

The double salt $PbI_2,KI,2H_2O$ has neither a proper melting point nor a proper solubility. It can only exist in contact with solutions in which the ratio of potassium to lead is greater than the ratio K : Pb. At elevated temperatures, the double salt in contact with the solution is decomposed into another double salt containing only half a molecule of water, the ratio of the two iodides being unknown. There is probably no temperature of transformation for either of these double salts into their components. J. W.

A New Double Salt. By W. MEYERHOFFER (*Monatsh.*, **13**, 716—741).—The author describes the methods by which he has determined the conditions under which the double salt, $CuCl_2,LiCl,2H_2O$, exists in contact with water. The results obtained are of no general interest.

G. T. M.

Graphochemistry of Lime Soda Glasses. By E. NICKEL (*Zeit. physikal. Chem.*, **10**, 450—453).—In this paper, the author applies the principles described in Abstr., 1892, 1158, to the discussion of the composition of lime soda glasses.

J. W.

Hydrates of Ferric Chloride. By H. W. B. ROOZEBOOM (*Zeit. physikal. Chem.*, **10**, 477—503).—The author has made a comprehensive investigation of the hydrates of ferric chloride, studying in especial the solubility curves of these hydrates in water. They are four in number, namely, $Fe_2Cl_6,12H_2O$; $Fe_2Cl_6,7H_2O$; $Fe_2Cl_6,5H_2O$, and $Fe_2Cl_6,4H_2O$. Only the first and third of these were previously known, the composition of the latter being uncertain. The hydrate $Fe_2Cl_6,7H_2O$ forms aggregates of small, well-characterised, monoclinic crystals, very strongly dichroïc, the colours varying between yellow and blue. They are much lighter in colour than those of the pentahydrate, and not nearly so deliquescent. The hydrate $Fe_2Cl_6.4H_2O$ forms rhombic crystals, showing a dichroïsm from yellow to brown.

The melting points of the four hydrates lie at 37°, 32·5°, 56°, and 73·5° respectively. Below these points, each can exist in equilibrium with solutions containing either more or less water than itself. These saturated solutions form two branches of the solubility curve, which join without a break at the melting point. The curve for the solutions of a hydrate containing more water than itself cuts at a definite point the curve for the solutions of the next higher hydrate containing less water than itself. At such points, the solutions solidify to mixtures of both hydrates. In the case of the extreme hydrates, ice appears on the one hand, and anhydrous ferric chloride on the other. These "cryohydric" points are at −55°, 27·4°, 30°, 55°, and 66°, respectively. Many phenomena of supersaturation were observed, all of which could be deduced from the nature of the solubility curves. The following determinations of the vapour pressure at 15° were made:—

	Vapour pressure in mm. mercury.
$Fe_2Cl_6,12H_2O$ with weaker solution	6·0
$Fe_2Cl_6,7H_2O$ „ „	2·3
$Fe_2Cl_6,12H_2O$ with $Fe_2Cl_6,7H_2O$.....	1·8
$Fe_2Cl_6,12H_2O$ with stronger solution	1·4
$Fe_2Cl_6,5H_2O$ with weaker solution	1·3

The heats of solution of the hydrates with 12, 7, and 5 mols. H_2O at 15° pass from positive to negative values with increasing concentration of the solution; in saturated solutions, they are negative, which corresponds with the increase of solubility with rise of temperature.

The following tables exhibit the composition of the various solutions in equilibrium with the solids mentioned:—

n' = mols. Fe_2Cl_6 to 100 mols. H_2O.
n'' = ,, H_2O ,, 1 mol. Fe_2Cl_6.

Ice.

t.	n'.	n''.
0°	0	∞
−10	1·00	100
−20·5	1·64	61
−27·5	1·90	52·6
−40	2·37	42·2
−55	2·75	36·4

$Fe_2Cl_6,5H_2O$.

t.	n'.	n''.
12°	12·87	7·77
20	13·95	7·17
27	14·85	6·73
30	15·12	6·61
35	15·64	6·40
50	17·50	5·71
55	19·15	5·22
56	20·00	5·00
55	20·32	4·92

$Fe_2Cl_6,4H_2O$.

t.	n'.	n''.
50°	19·96	5·01
55	20·32	4·92
60	20·70	4·88
69	21·53	4·64
72·5	23·35	4·28
73·5	25·00	4·00
72·5	26·15	3·82
70	27·90	3·58
66	29·20	3·43

$Fe_2Cl_6,7H_2O$.

t.	n'.	n''.
20°	11·35	8·81
27·4	12·15	8·23
32	13·55	7·38
32·5	14·29	7·00
30	15·12	6·61
25	15·54	6·47

$Fe_2Cl_6,12H_2O$.

t.	n'.	n''.
−55°	2·75	36·4
−41	2·81	35·6
−27	2·98	33·6
0	4·13	24·2
10	4·54	22·0
20	5·10	19·6
30	5·93	16·9
35	6·78	14·8
36·5	7·93	12·6
37	8·33	12·0
36	9·29	10·8
33	10·45	9·57
30	11·20	8·92
27·4	12·15	8·23
20	12·83	7·80
10	13·20	7·57
8	13·70	7·30

Fe_2Ci_6.

t.	n'.	n''.
66°	29·20	3·43
70	29·42	3·40
75	28·92	3·46
80	29·20	3·43
100	29 75	3·33

J. W.

Anhydrous and Crystalline Iron Fluorides. By G. Poulenc (*Compt. rend.*, **115**, 941—944).—Ferrous fluoride, FeF_2, made by passing air-free hydrogen fluoride over red-hot iron or anhydrous ferric chloride, crystallises in small, branching, colourless, rhombic prisms, which turn yellow on exposure to the air. The sp. gr. is 4·09. When heated with sulphuric acid, sodium carbonate, air, hydrogen, steam, or hydrogen chloride, it is decomposed, the reaction in the last-named case being the reverse of that involved in its formation. Ferric fluoride, Fe_2F_6, is prepared by passing hydrogen fluoride over red-hot iron, ferric oxide, hydrated ferric fluoride, or ferric chloride, or by projecting the hydrated fluoride into fused ammonium chloride, and heating the product in a current of inert gas. It does not fuse, even at 1000°, although it partially volatilises and partially crystallises at that temperature, forming small, highly refractive, greenish crystals of sp. gr. 3·87. It is only slightly attacked by nitric, hydrochloric, and sulphuric acids, but is decomposed into ferric oxide by heating in contact with air, and is reduced by hydrogen at a dull-red heat. When heated in steam, it is decomposed into ferric oxide and hydrogen fluoride, whilst with hydrogen chloride or sulphate, ferrric chloride or sulphate and hydrogen fluoride are formed. It is decomposed also by fusion with sodium carbonate. Jn. W.

Preparation of Metallic Chromium by Electrolysis. By E. Placet (*Compt. rend.*, **115**, 945).—The solution to be electrolysed contains chrome alum and an alkali sulphate, and is acidified with sulphuric acid. The metallic chromium is deposited at the cathode as a hard, bluish-white, lustrous metal, which, under certain conditions, crystallises in groups resembling the branching of firs. It does not oxidise in the air, and is not attacked by strong nitric or sulphuric acid or potash. Other metals may be plated with chromium, and the surface so obtained resembles "oxidised" silver. Chromium forms many alloys. Jn. W.

Cryoscopic Behaviour of Aqueous Solutions of the Violet and Green Chromic Chlorides. By G. Marchetti (*Real. Accad. Linc.*, 1892, i, 215—217, and *Gazzetta*, **22**, ii, 375—379).—The author has prepared the violet and green modifications of chromic chloride by Recoura's method (Abstr., 1886, 508), and finds them to have the composition $Cr_2Cl_6,12H_2O$ when dried over sulphuric acid, not $Cr_2Cl_6,13H_2O$, as found by Recoura.

The molecular depression of the freezing point of water by the two chlorides is very different; that caused by the violet modification being much the greater. The hydrolytic dissociation is far advanced in both cases; the molecular depression for the violet modification is approximately equal to that obtained with ferric chloride.

W. J. P.

Complex Acids containing Heptavalent Iodine. By C. W. Blomstrand (*Zeit. anorg. Chem.*, **1**, 10—50; compare Abstr., 1887, 327; 1890, 107).—The author first discusses the probability of the iodine atom in periodic acid being septavalent, and compares it with the quinquevalent phosphorus atom in phosphoric acid, which acid

contains the tervalent group PO, just as periodic acid contains the quinquevalent group IO. He then shows that this view of the constitution of periodic acid affords an explanation of the constitution of the salts of certain complex acids which he has prepared, which contain periodic acid united with varying quantities of molybdic acid. These salts may be divided into three groups derived respectively from *hexamolybdoperiodic acid*, $IO(OH)_2(O{\cdot}MoO_2{\cdot}O{\cdot}MoO_2{\cdot}OH)_3$, *monomolybdoperiodic acid*, $IO(OH)_4{\cdot}O{\cdot}MoO_2{\cdot}OH$, and *tetramolybdoperiodic acid*, $IO(OH)_3(O{\cdot}MoO_3{\cdot}O{\cdot}MoO_2{\cdot}OH)_2$.

Hexamolybdoperiodates.—These were prepared by heating the periodate of the metal, or periodic acid itself, with molybdic acid and the carbonate of the metal in water until solution had taken place, and allowing the resulting solution to crystallise, best at the ordinary temperature. They were also obtained by making a dilute solution of the free acid from barium molybdate, periodic acid, and sulphuric acid, and neutralising this solution with the carbonate of the metal. This dilute aqueous solution of the free acid, when evaporated, yielded a transparent, amorphous mass, without a trace of crystalline structure. The *sodium salt*, $Na_5Mo_6IO_{24}$, crystallises with $17H_2O$ in rhombohedra, $a : c = 1 : 1{\cdot}9635$, and with $13H_2O$ in triclinic plates, $a : b : c = 1{\cdot}0557 : 1 : 1{\cdot}1072$; $\alpha = 127°\ 57'$, $\beta = 60°\ 51'$, $\gamma = 79°\ 37'$. The *potassium*, or more strictly *potassium hydrogen salt*, $K_5Mo_6IO_{24} + K_4HMo_6IO_{24} + 12H_2O$, forms four- or six-sided triclinic plates, somewhat analogous to, but not isomorphous with, those of the sodium salt, $a : b : c = 0{\cdot}7497 : 1 : 0{\cdot}9708$; $\alpha = 101°9\frac{1}{2}'$, $\beta = 68°\ 10'$, $\gamma = 80°\ 34'$. The *lithium salt*, $Li_5Mo_6IO_{24}$, crystallises with $15H_2O$ in a rhombohedral form, $a : c = 1 : 1{\cdot}8823$, and with $9H_2O$ in a second form with prismatic habit, which could not be determined crystallographically. The *ammonium salt*, $(NH_4)_5MoIO_{24} + 6H_2O$, crystallises in two triclinic varieties, of which the first and most commonly occurring is isomorphous with the potassium salt, while the second forms hexagonal plates; (1.) $a : b : c = 0{\cdot}7417 : 1 : 0{\cdot}9550$; $\alpha = 122°\ 43'$, $\beta = 69°\ 2'$, $\gamma = 75°\ 29\frac{1}{2}'$; (2.) $a : b : c = 0{\cdot}4973 : 1 : 0{\cdot}5770$; $\alpha = 83°\ 35'$ $\beta = 86°\ 17'$ $\gamma = 78°\ 4'$. *Calcium salts.*—$Ca_5(Mo_6IO_{24})_2 + 26H_2O$, forms ill-defined crystals; $Ca_2HMo_6IO_{24} + 10H_2O$, slender prisms. The *strontium sodium salt*, $Sr_2NaMo_6IO_{24} + 10H_2O$, forms crusts of microscopic prisms. The *barium sodium salt*, $Ba_5(Mo_6IO_{24})_2 + 2Ba_2NaMo_6IO_{24} + 28H_2O$, also forms long prisms. The *manganese sodium salt*, $MnNa_3Mo_6IO_{24} + 16H_2O$, forms apparently rhombohedral crystals. These last three salts were prepared by the addition of strontium, barium, and manganese chlorides respectively to a solution of the sodium salt.

Ammonium sodium monomolybdoperiodate, $(NH_4)_2NaH_2MoIO_9 + 4H_2O$, is obtained by treating the sodium hexa-salt with ammonia; it crystallises in quadrangular, triclinic plates similar to, if not isomorphous with, the potassium and sodium hexa-salts, $a : b : c = 0{\cdot}6953 : 1 : 0{\cdot}8662$; $\alpha = 97°\ 7'$, $\beta = 75°\ 30'$, $\gamma = 80°\ 36'$.

Ammonium tetramolybdoperiodate, $(NH_4)_4HMo_4IO_{18} + 3H_2O$, is obtained by treating the ammonium salt of the hexa-acid with ammonia; it forms prismatic crystals. C. F. B.

Action of Hydrogen Peroxide on certain Fluorides and Oxyfluorides. By A. Piccini (*Zeit. anorg. Chem.*, **1**, 51—64).—Compounds are formed which contain oxygen in the same state as in hydrogen peroxide; it is given off when the compound is heated or treated with permanganate. *Potassium fluoroxypermolybdate*, $MoO_3F_2,2KF + H_2O$, was prepared by dissolving the fluoroxymolybdate, $MoO_2F_2,2KF + H_2O$ (obtained by treating molybdic acid with hydrofluoric acid and potassium fluoride), in 4 per cent. hydrogen peroxide, and recrystallising the product from aqueous hydrogen peroxide containing a little hydrofluoric acid. It forms yellow, transparent, monoclinic tables, $a : b : c = 1{\cdot}2394 : 1 : 1{\cdot}9928$; $\beta = 50° 28'$, is stable in air, loses water, at 100°, oxygen at 150°, and, when heated in air, yields potassium molybdate, $KMoO_4$, when in a vacuum, the fluoroxymolybdate, $Mo_2F_2,2KF$. *Rubidium fluoroxypermolybdate*, $MoO_3F_2,2RbF + H_2O$, was prepared by adding a hydrofluoric acid solution of molybdic acid to a hydrogen peroxide solution of rubidium chloride. It forms long, narrow plates or prisms which are monoclinic, $a : b : c = 1{\cdot}27415 : 1 : 2{\cdot}0619$, and isomorphous with the potassium salt, which it resembles in its properties. *Cæsium fluoroxypermolybdate*, $MoO_3F_2,2CsF + H_2O$ (?), prepared like the rubidium salt, forms yellow plates which probably have the composition given. *Triammonium fluoroxypermolybdate*, $MoO_3F_2,3NH_4F$, is formed by adding hydrogen peroxide and an excess of ammonium fluoride to a hydrofluoric acid solution of ammonium molybdate; also by the action of hydrogen peroxide on both of the fluoroxymolybdates $MoO_2F_2,3NH_4F$ and $MoO_2F_2,2NH_4F$. It forms sometimes pointed, sometimes flattened, yellow prisms, which, when heated above 100°, lose weight, and leave a residue of molybdic anhydride. C. F. B.

Fluoroxymolybdates: the Non-existence of Cuprous Fluoride. By F. Mauro (*Real. Accad. Linc.*, 1892, i, 194—203).—*Cupric fluoroxymolybdate*, $MoO_2F_2,CuF_2,4H_2O$, separates in transparent, blue, six-sided plates from a hydrofluoric acid solution of molybdic anhydride and copper oxide in molecular proportion; the crystals are monosymmetric, $a : b : c = 1{\cdot}4828 : 1 : 1{\cdot}0987$, $\beta = 85° 9'$. The substance is unaltered by dry air, but readily absorbs moisture from the atmosphere, yielding a pasty mass, which subsequently dries, leaving a blue powder. The crystals lose weight and become light green at 115°, and begin to evolve hydrogen fluoride at 135°.

Cupric fluoroxyhypomolybdate, $MoOF_3,CuF_2,4H_2O$, is prepared by heating cuprous oxide with a solution of molybdic anhydride in hydrofluoric acid in an atmosphere of carbonic anhydride, the solution being first reduced electrically as in the preparation of the fluoroxyhypomolybdates of potassium and ammonium (Abstr., 1890, 702); the solution deposits a mixture of red octahedra of metallic lustre, now under examination, and cupric fluoroxyhypomolybdate. The latter forms blue, monosymmetric crystals, $a : b : c = 1{\cdot}4745 : 1 : 1{\cdot}0929$, $\beta = 85° 43'$, which deliquesce in the air with separation of metallic copper; it crystallises unchanged from hydrofluoric acid, but is decomposed by water, copper being deposited. The salt possesses reducing properties, as do all the fluoroxyhypo-

molybdates, and is similar in crystalline form to cupric fluoroxymolybdate.

Cuprous fluoride cannot be prepared by the method given by Berzelius (*Ann. Phys. Chem.*, **1**, 28). The many attempts made by the author to prepare cuprous fluoride in various ways merely gave metallic copper; there is little doubt but that the substance obtained by Berzelius was the impure metal.

Zinc fluoroxyhypomolybdate, $MoOF_3,ZnF_2,6H_2O$, separates in transparent, blue crystals of vitreous lustre from a solution of zinc oxide (1 mol.) in an electrically reduced solution of molybdic anhydride (1 mol.) in hydrofluoric acid. The crystals rapidly deliquesce in the air, forming a dark blue paste; they belong to the rhombohedral system $a : c = 1 : 0{\cdot}5136$ or $\xi = 112° 51'$, and present the same crystallographic properties as the corresponding fluorosilicates, fluorostannates, and analogous salts. Tables are given showing the crystallographic resemblances between the above and similar salts.

W. J. P.

Preparation of Tungstates free from Molybdenum. By C. Friedheim and R. Meyer (*Zeit. anorg. Chem.*, **1**, 76—81).—Commercial tungstates and tungstic acid contain varying quantities of molybdenum. After several unsuccessful attempts to get rid of this impurity, the following method was found to give the desired result. Sodium tungstate, prepared in the usual way, is dissolved in cold water, and to the saturated solution hydrochloric acid is added until the reaction is only feebly alkaline; the paratungstate thus obtained is crystallised out and once recrystallised. One half of it is dissolved in boiling water, and hydrochloric and a little nitric acid added; hydrated tungstic acid is precipitated. This is washed thoroughly with hot water and added to a boiling solution of the other half of the paratungstate, until a portion no longer gives a precipitate with hydrochloric acid. The bulk of the solution is then filtered, hydrochloric acid is added, and the solution is boiled and repeatedly saturated with hydrogen sulphide. This precipitates the molybdenum as sulphide, whilst the metatungstate is not attacked. The solution is filtered, concentrated, oxidised with a few drops of bromine water, and neutralised with soda; pure sodium paratungstate can then be obtained from it by crystallisation. To obtain the potassium and ammonium salts, the acid should be prepared by adding hydrochloric acid to the sodium salt, and then neutralised with potash or ammonia.

An analysis of sodium paratungstate thus prepared agreed better with the formula $5Na_2O,12WO_3,28H_2O$ than with $3Na_2O,7WO_3,16H_2O$.

C. F. B.

Crystallised Sodium Titanates. By H. Cormimbœuf (*Compt. rend.*, **115**, 823—825).—The titanates $2Na_2O,3TiO_2$; $Na_2O,2TiO_2$, and $Na_2O,3TiO_2$ are obtained by heating the titanate $3Na_2O,2TiO_2$, with sodium tungstate containing various proportions of free tungstic acid.

The sesquititanate is obtained in short hyaline or milk-white prisms by heating 5 parts of normal sodium tungstate at 800° for 10 hours with a previously fused mixture of 1 part of titanic anhydride and

2 parts of sodium carbonate. The crystals are optically active, belong to the monoclinic system, and are macled after the manner of felspars; they are insoluble in water, but dissolve slowly in cold hydrochloric acid and more rapidly on heating.

The bititanate is obtained in imperfect crystals of similar form by heating 20 parts of normal sodium tungstate and 5 parts of tungstic anhydride with a previously fused and finely powdered mixture of 4 parts of titanic anhydride and 8 parts of sodium carbonate. The crystals are insoluble in water and are very slowly attacked by cold hydrochloric acid, but dissolve rapidly when heated with this acid.

The trititanate is obtained in long, highly birefractive needles by heating 10 parts of normal sodium tungstate and 5 parts of tungstic anhydride with a previously fused mixture of 2 parts of titanic anhydride and 4 parts of sodium carbonate. It is almost insoluble in boiling hydrochloric acid, and in sulphuric acid it dissolves about as readily as titanic anhydride.

When the composition of the fused tungstate approaches that of the normal tungstate, rutile separates instead of a titanate. The acid titanates seem unable to take up a further quantity of base, even when fused with highly basic tungstates. C. H. B.

Action of Antimony on Hydrochloric acid. By A. Ditte and R. Metzner (*Compt. rend.*, **115**, 936—939).—Pure antimony, precipitated by tin from an acid solution of the trichloride, does not attack hydrochloric acid of any strength at any manageable temperature, even in the presence of platinum or gold chloride. In the presence of oxygen, however, the metal is slowly dissolved, but the dissolution takes place with equal facility in the absence of the acid. Jn. W.

Double Halogen Compounds of Gold. By E. Petersen (*J. pr. Chem.* [2], **46**, 328—335).—Krüss and Schmidt (Abstr., 1888, 28, 1256) maintain that there are no such compounds as Au_2Cl_4 and Au_2Br_4, the products of the action of chlorine and bromine on gold being a mixture of unaltered metal with the trichloride and tribromide respectively. The author points out that water or ether, as employed by Krüss and Schmidt, to wash out the trichloride or tribromide is inadmissible, inasmuch as the dichloride and dibromide are decomposed thereby. He uses dry absolute alcohol at $-20°$ as a solvent for any trichloride, and he obtains considerable evidence that even with this the dichloride is being slowly decomposed. The experiments with chlorine were conducted substantially as directed by Thomsen (Abstr., 1888, 559), and they led the author to conclude that by the action of a rapid current of chlorine on finely-divided gold, without the application of external heat but with provision for retaining the heat developed, aurosoauric chloride, Au_2Cl_4, together with a small quantity of auric chloride, is formed. This conclusion was confirmed by a thermochemical investigation.

The evidence in favour of Au_2Br_4 was not so good, inasmuch as no solvent for the tribromide could be found which would not decompose the tribromide; but, considered in conjunction with a thermochemical

investigation, it was sufficient to justify the author in concluding that aurosoauric bromide also has a separate existence.

A. G. B.

Some Platinum-Ammonium Compounds. By O. CARLGREN and P. T. CLEVE (*Zeit. anorg. Chem.*, **1**, 65—75).—By the action of a boiling solution of sulphurous anhydride on the iodonitrate, $\begin{matrix}NH_3\\|\\NH\end{matrix}>PtI\cdot NH_3\cdot NH_3\cdot NO_3$, the following two complex crystalline substances are formed:—

A. $\left(\begin{matrix}NH_3\\|\\NH\end{matrix}>PtI\cdot NH_3\cdot NH_3\right)_2SO_4 + Pt<\begin{matrix}NH_3\cdot NH_3\\NH_3\cdot NH_3\end{matrix}>SO_4.$

B. $PtSO_3 + 3Pt<\begin{matrix}NH_3\cdot NH_3\\NH_3\cdot NH_3\end{matrix}>SO_3 + 4H_2O.$

A forms star-shaped groups of ill-defined, colourless or pale yellow crystals. When treated with hydrochloric acid, it yields *platodiamine chloride*, $Pt(NH_3\cdot NH_3\cdot Cl)_2$ and *platinodiamine iodochloride*,

$$Pt(NH_3\cdot NH_3Cl)_2ClI;$$

the former in colourless needles, the latter in brown crystals. When heated with 3 per cent. hydrogen peroxide, it yields *iodohydroxyplatinodiamine sulphate*, $HO\cdot PtI<\begin{matrix}NH_3\cdot NH_3\\NH_3\cdot NH_3\end{matrix}>SO_4 + H_2O$, and *hydroxyplatinodiamine sulphate*, $Pt(OH)_2<\begin{matrix}NH_3\cdot NH_3\\NH_3\cdot NH_3\end{matrix}>SO_4 + 4HO$; the first in small, reddish-brown combinations of the cube with the octahedron, the second in long, colourless needles with inclined end faces, and also crystallised with $1H_2O$, in large, colourless plates. When treated with silver nitrate, it yields silver iodide, and a compound $\left(Pt<\begin{matrix}NH_3\cdot NH_3\\NH_3\cdot NH_3\cdot NO_3\end{matrix}\right)_2SO_4 + Pt<\begin{matrix}NH_3\cdot NH_3\\NH_3\cdot NH_3\end{matrix}>SO_4$, in star-shaped groups of tetragonal plates ($a : c = 1 : 1{\cdot}0257$).

B, when treated with silver nitrate, yields two crystalline compounds, $PtSO_3 + 3Ag_2SO_3$, and $Pt(NH_3\cdot NH_3\cdot Cl)_2$, the first directly, as a white precipitate, the second (platodiamine chloride) when the solution filtered from this precipitate is treated with hydrochloric acid.

The action of hydrogen peroxide on certain compounds was then studied. *Hydroxyplatinodiamine chloride*, $Pt(OH)_2(NH_3\cdot NH_3Cl)_2$, was obtained both by decomposing the sulphate with barium chloride and by the action of hydrogen peroxide on platodiamine chloride; it forms small, colourless, tabular, monoclinic crystals, $a : b : c = 1{\cdot}5310 : 1 : 0{\cdot}6702$. The *bromide* and *iodide*, with analogous formulæ, were prepared from the sulphate by the action of barium bromide and iodide respectively; the first forms short, colourless prisms with pyramidal end faces, the second tiny, hexagonal prisms. The *nitrite*, $Pt(OH)_2(NH_3\cdot NH_3\cdot NO_2)_2$, was obtained by the action of silver nitrite upon the chloride; it crystallises in needles, and explodes when heated. The *nitrate*, $Pt(OH)_2(NH_3\cdot NH_3\cdot NO_3)_2$, obtained from the sulphate and barium nitrate, or from platodiamine nitrate and hydrogen peroxide,

forms dendritic aggregates of flat, rhombic tables, and explodes when heated. The *sulphate*, $Pt(OH)_2(NH_3{\cdot}NH_3)_2SO_4$, was obtained by the action of hydrogen peroxide on platodiamine sulphate, both crystallised with $4H_2O$, as described above, and anhydrous in small prisms. The *dichromate*, $Pt(OH)_2(NH_3{\cdot}NH_3)_2Cr_2O_7$, was obtained by the action of hydrogen peroxide on the precipitate formed when potassium dichromate is added to platodiamine chloride. It is a lemon-yellow powder which explodes when heated. C. F. B.

Mineralogical Chemistry.

Vanadiferous Lignite in the Argentine Republic. By J. J. J. Kyle (*Chem. News*, **66**, 211—212).—A seam of lustrous, non-fibrous, very brittle, black, bituminous coal has been discovered near the town of San Raphael, province of Mendoza, Argentine Republic. The sp. gr. of the coal is 1·173, and its proximate composition :—

Loss at 100°	2·05
Volatile matters	49·51
Fixed carbon	47·81
Ash	0·63
	100·00

The ash is greenish, and has the following percentage composition :—

Soluble in acid.		Insoluble in acid.		Undetermined.	
V_2O_5	38·22	SiO_2	13·70	Traces of Mn,	
P_2O_5	0·71	Fe_2O_3	9·42	MgO, Cl, and	
SO_3	12·06	Al_2O_3	5·26	loss,	1·33
CaO	8·44	MgO	0·83		
Fe_2O_3	4·98				
Al_2O_3	3·32				
K_2O	1·73				

The vanadium is nearly all soluble in alkali, and would seem, therefore, to be present in the ash chiefly as the uncombined pentoxide, partly as potassium vanadate, some, also, as iron or aluminium vanadate; and, inasmuch as a ton of this coal would yield $4\frac{1}{4}$ lbs. of vanadium, it must be regarded as a rich source of vanadium compounds. D. A. L.

Artificial Production of Zircon. By K. v. Chroustchoff (*Jahrb. f. Min.*, 1892, ii, Mem. 232—236).—The author describes an apparatus he has devised for heating aqueous solutions to a red heat. Unlike that employed by Friedel and Sarasin, which consisted of a steel tube closed at both ends by platinum plates, it is closed at one

end only, and consists of a cylindrical platinum crucible enclosed in a cast-steel block, the lid being screwed down in such a manner as to withstand great pressure. Hitherto but two experiments have been made with this apparatus.

In the first experiment, the crucible was charged with gelatinous silica, gelatinous alumina, and gelatinous zirconium hydroxide. It was subjected to a gradually increasing heat for six days, and allowed to cool. The residue in the crucible was then found to consist of a white powder, in part distinctly crystalline. The crystals exhibited, under the microscope, hexagonal forms, and had a sp. gr. of 2·87. On analysis, they yielded—

SiO_2.	Al_2O_3.	ZrO_2.	H_2O.	Total.
53·65	23·76	14·54	7·86	99·81

A mineral of this composition is unknown in nature. It may, however, be described as a zirconia-bearing pyrophyllite.

In the second experiment, the crucible was charged with gelatinous silica and gelatinous zirconium hydroxide, and hermetically sealed. It was heated for two hours by 12 bunsen burners. On cooling, it was found that no water had escaped. The crystals obtained were mostly pyramidal, and gave, on analysis, 32·84 per cent. of silica and 67·17 per cent. of zirconia. B. H. B.

Cobaltiferous Chalybite from Neunkirchen. By G. Bodländer (*Jahrb. f. Min.*, 1892, ii, Mem. 236).—A red mineral, occurring in thin layers on quartz at the cobalt mine, near Neunkirchen, in the Siegen district, gave, on analysis, the following results:—

FeO.	CaO.	MgO.	CoO.	CO_2.
54·34	1·21	8·80	3·85	41·55

The mineral is thus a spathic iron ore containing isomorphous admixtures of carbonates of calcium, magnesium, and cobalt, its red colour being due to the last named. B. H. B.

Crystallised Slags from Raibl. By P. P. Heberdey (*Zeit. Kryst. Min.*, **21**, 56—73).—The author has made a chemical and crystallographical examination of a series of slags from the Raibl lead works, collected for the University of Vienna. The results are of interest in that an artificial lead zinc chrysolite has been observed, the existence of which has hitherto been unknown. Analysis shows this mineral to have the formula $Pb_{10}Zn_7Mg_2FeSi_{10}O_{40}$.

In an appendix to the paper, the author gives analyses of the dolomite in which the Raibl galena deposits occur. In this dolomite, he has detected distinct traces of thallium and of lithium.

B. H. B.

Artificial Production of Garnet (Melanite) and Sphene. By L. Michel (*Compt. rend.*, **115**, 830—832).—An intimate mixture of 10 parts of titaniferous iron ore, 10 parts of calcium sulphide, 8 parts of silica, and 2 parts of carbon was heated in a graphite crucible at a

temperature of 1200° for about five hours, and allowed to cool very slowly. The lower part of the regulus consists of the iron sulphide Fe_4S_3, with some granules of iron carbide; the upper part is of porous texture, and contains vesicles which enclose crystals of garnet (melanite), sphene, and the iron sulphide.

The garnet is obtained in rhomboidal dodecahedra about 0·5 mm. in diameter; hardness 7; sp. gr. 3·8. They are dark brown with a vitreous lustre, melt to a black magnetic glass, and have the composition SiO_2, 36·45; Fe_2O_3, 29·80; and CaO, 32·65 = 98·90.

The artificial sphene forms translucid, monoclinic prisms, elongated along $h'g'$ or (100)(010), the angle mm or (110)(1$\bar{1}$0) being 113° 26′, whilst that of the natural crystals is 113° 31′. They attain a length of 4 mm., have a strong, positive birefraction with the plane of the optical axes in g', a reddish-brown colour, and an adamantine lustre; hardness 5; sp. gr. 3·4. Their composition is SiO_2, 32·10; TiO_2, 40·00; CaO, 27·14; Fe_2O_3, traces = 99·24.

Both garnet and sphene have previously been obtained artificially, but never by this method, and in one operation.

The iron sulphide Fe_4S_3 was obtained in small crystals which seemed to belong to the rhombic system, and were identical in their properties with those obtained by Gautier and Hallopeau (Abstr., 1889, 677). C. H. B.

Friedelite from the Sjö Mine, Sweden. By L. J. Igelström (*Zeit. Kryst. Min.*, **21**, 92—95).—Friedelite has been found by the author at the Sjö mine, Örebro, Sweden, in association with hausmannite and braunite. An analysis of the mineral gave the following results:—

SiO_2.	Cl.	MnO.	FeO.	CaO.	MgO.	Mn.	H_2O.	Total.
34·36	3·00	45·88	1·35	1·50	1·50	2·79	9·00	99·38

The results are in perfect accord with those of analyses of friedelite from Adervielle, in the Pyrenees, and from Harstigen, in Sweden, the two other localities at which this interesting mineral has been observed. B. H. B.

Minerals of the Pyroxene Group. By A. Schmidt (*Zeit. Kryst. Min.*, **21**, 1—55).—In this lengthy paper, the author gives the results of a careful crystallographical investigation of the members of the monosymmetrical series of the pyroxene group which are usually known as diopsides. His researches were conducted with the following minerals:—Diopside from the Ala Valley, the white and green diopsides from Achmatowsk, the diopsides from Nordmarken and from the Ziller Valley, and, lastly, the augites of the Arany Mountains. B. H. B.

Chemical Constitution of Hornblende. By H. Haeffcke (*Jahrb. f. Min.*, 1892, ii, Ref. 404—406).—The author has analysed eight specimens of hornblende, all of which were found to contain alkalis. According as they are free from sesquioxides or not, they

appear to be isomorphous mixtures of bisilicates or of normal silicates. In almost all cases the results were influenced by the presence of large amounts of mica in the hornblendes examined, so that the existence of hornblende formed exclusively from normal silicates is still open to question. B. H. B.

Physiological Chemistry.

Influence of Light on Gas Exchange. By C. A. Ewald (*J. Physiol.*, **13**, 847—859).—Taking the average of 17 experiments, the carbonic anhydride excreted by curarised frogs in the light exceeds that produced in the dark by less than 2 per cent., the ratio being 100 : 98·5. If two series are thrown out, where slight muscular movements occurred, the animals being incompletely under the influence of the drug, the ratio of the remaining 15 is 100 : 99, a difference which comes within experimental error. Muscular action being eliminated, light does not in any appreciable way influence the excretion of carbonic anhydride. W. D. H.

Gaseous Tension in the Blood and Serum of Peptonised Animals. By V. Grandis (*Real. Accad. Linc.*, **7**, ii, 471—478).—By the peptonisation of animals, the blood acquires the property of giving up a larger quantity of carbonic anhydride than usual in its passage through the lungs. The gaseous tension and other properties of the blood were examined in Gaule's apparatus, and in order to ensure absence of oxygen, the blood was drawn from the asphyxiated animal; the gas obtained in this way consisted principally of carbonic anhydride mixed with a little nitrogen. Comparative experiments were made on dogs both before and after injection of the peptone solution. It was found that blood drawn from the right auricle has a greater gaseous tension than normal blood from the same source; the reverse is true of blood drawn from the carotid.

Experiments on the amount of free and combined carbonic anhydride in the serum of peptonised blood, show that the former is slightly greater than in the normal blood serum; the quantity of combined carbonic anhydride in the serum is considerably diminished by peptonisation. Tables are given supporting the author's conclusions. W. J. P.

Elimination of Carbonic Oxide. By L. de Saint-Martin (*Compt. rend.*, **115**, 835—839).—Rabbits were allowed to breathe for 15 to 20 minutes, through a canula inserted in the trachea, a mixture of 2 litres of oxygen with 70 c.c. of carbonic oxide, and the quantity of oxygen absorbed was determined by analysis of the gas remaining in the flexible india-rubber bag in which the original mixture was contained. The rabbits were then allowed to breathe pure oxygen, the exhaled gas being all collected, and the carbonic oxide in it estimated.

The elimination is at first very rapid, but quickly diminishes, becoming very slight at the end of the third hour. From 5 to 6 per cent. of the absorbed carbonic oxide is, however, never eliminated as such, but undergoes alteration in the living tissues, and is probably converted into carbonic anhydride. C. H. B.

Influence of Increased or Diminished Consumption of Food and of the Salts added to the Food, on Digestion and Resorption. By H. Weiske (*Landw. Versuchs-Stat.*, **41**, 145—164).—In order to ascertain the power of digestion and resorption for oats, the solid excrement of five of the rabbits used in the last experiment (Abstr., 1892, 647), namely, *K* (fed with oats alone), *M* (fed with oats and calcium phosphate), *J* (oats and sodium hydrogen phosphate), *O* and *N* (oats and sodium citrate), was collected for sixteen successive days, weighed, and analysed. The amount of proteïn differed considerably, being least in *K* and *M* (4·75 and 5·25 per cent.), and highest in *O*, *N*, and *J* (10·81 per cent.). *J* gave also the highest amount of ether extract (4·07), *N* and *O* the least (1·74 and 1·55 per cent.). The amounts of substance soluble in warm water and in artificial gastric juice were also determined: the amount of soluble substance (in water) was nearly twice as much in the case of the excrement from *J* as in the others, whilst the substance soluble in gastric juice was much greater in *N* and *O* than in *K* and *M*. The amount of food consumed by the five rabbits during the experiment was about equal, amounting (for the 16 days) to 884—890 grams of air-dry oats. For *M*, the food was about sufficient, whilst all the others lost weight, *K* 125, *J* 540, *N* 885, and *O* 300 grams, in three months. When the results with *K* (which had no salts) are compared with an earlier experiment (*Landw. Jahrb.*, **21**, 796), in which the rabbit was similarly fed, except that it had 100 grams of oats daily, instead of 55·5 grams, as in these experiments, a great difference is found in the digestion coefficients (except ether extract), indicating that with the same foods the amounts digested are much less when large amounts of food are consumed. Tables are given showing the digestion coefficients obtained with the five rabbits; there are differences, but they are not great, and are, moreover, irregular, except as regards the proteïn, which is highest in the case of *K*, the next highest being *M*, whilst *J*, *N*, and *O* differ most from *K*.

A fresh series of experiments was made, in which five rabbits, about seven months old, were fed with oats, *ad libitum*; four of them, Nos. 2—5, having, respectively, each day, 0·1, 0·25, 0·5, and 0·75 gram of sodium citrate; No. 1 having none. Each of the rabbits consumed 1 kilo. of oats in 10 days, after which their appetites began to fail, especially in the case of 4 and 5. Tables are given showing the amounts of oats consumed during the whole period of 49 days, the increase of weight, and the weight and composition of the excrement of each rabbit. The digestion coefficients show only slight differences, as if the addition of sodium citrate had been without effect. But when the amounts of food consumed daily are considered, it is seen that the presence of citrate in Experiments 2—5 caused an

increasing diminution in the amount of food consumed, and that instead of the food being more completely digested, as the amount diminished (as was observed when different amounts of oats, both without salts, were consumed), the using up of the food was the same.

An examination of the blood of the rabbits at the end of the experiment gave the following results:—No. 1 contained 5·78 per cent., No. 5, 5·90 per cent. of ash. The ash contained—

	K_2O per cent.	Na_2O per cent.	CaO per cent.
1.	21·68	38·24	1·14
5.	18·63	35·65	0·68

results which agree with those of W. Beckmann, who found that sodium citrate had the power of withdrawing sodium and potassium, &c., from the body. N. H. M.

Proteïds of Kidney and Liver Cells. By W. D. Halliburton (*J. Physiol.*, **13**, 806—846).—Contrasting the proteïds found in the liver and kidney with those found in the simpler animal cells, such as lymph cells (Abstr., 1888, 974), the following general conclusions are arrived at:—

1. Albumin is either absent (kidney) or present in the merest traces (liver, lymph cells).

2. The proteïds present fall into two classes; nucleo-albumins and globulins.

3. The nucleo-albumin of lymph cells, and of the kidney, is obtainable by two methods: (*a.*) The finely-divided organ is extracted with distilled water for 24 hours, and this solution precipitated by weak acetic acid. The substance so obtained, called "tissue fibrogen," by Wooldridge, is a mixture or loose compound of nucleo-albumin with lecithin. (*b.*) The finely-divided organ is ground up in a mortar with sodium chloride, and the resulting viscous mass poured into excess of distilled water. The nucleo-albumin rises to the surface of the water. That the material prepared by the two methods is identical is shown by—

i. The result of gastric digestion, leading to an insoluble residue of nuclein. ii. After extraction of the organ by one method, the residue yields only traces by the other. iii. The heat coagulation temperature is the same, namely, 63—65°, in the case of the kidney. iv. Phosphorus estimation in both cases gives the same result; in the case of the kidney 0·37 per-cent.

4. The liver nucleo-albumin is obtainable in small quantities only, and only by the first method just described; it is remarkable for its high percentage of phosphorus, 1·45 per cent.

5. All these produce intravascular clotting when injected into the circulation in rabbits. They do so even after the removal of the lecithin. This may be because nucleo-albumin is the mother substance of fibrin ferment (Pekelharing, Abstr., 1892, 1112); or partly because these substances dissolve the white corpuscles.

6. The nucleo-albumins give none of the reactions of a proteose or peptone (compare Wright, Abstr., 1892, 646).

7. In all these varieties of cells there is a globulin which is coagulated by heat at about 48—50°. There is, in addition to this, in the liver cells, a globulin, which is coagulated by heat at about 70°.

8. Peptone, proteose, pepsin, myosin, and mucin are absent from both liver and kidney cells.

9. The proteïd formerly called cell-globulin β by the author is a nucleo-albumin, although whether it is the same as, or different from, that already mentioned, must be subject of renewed research.

10. Liver and kidney, when fresh and blood-free, have an alkaline reaction. Like muscle and lymph cells, they turn acid in a short time. W. D. H.

Mucin in Bone. By R. A. Young (*J. Physiol.*, **13**, 803—805).—Ebner (*Arch. milr. Anat.*, **29**) having shown the close analogy of the decussating fibres in bone to the white fibres of connective tissue, and that they are not calcified, it appeared necessary to investigate whether the matrix in which they are imbedded is completely calcified or not. This question may be most readily solved by ascertaining whether mucin, the most abundant constituent of the uncalcified matrix of connective tissue, is present or absent. The dense compact tissue of bone was used (care being taken to strip off all the periosteum), and not the spongy bone, as it is very difficult to free the latter from admixture with marrow, and it has been shown by Rustitzky (*Centr. med. Wiss.*, 1872, 562) that the marrow of some bones yields mucin. The bone was used either in the form of fine shavings or in powder, and was covered with excess of lime water or baryta water (diluted with 4 parts of water). The mixture was left for three or four days (being frequently stirred), and then filtered. The filtrate was treated with acetic acid of various strengths, but in no case was there any precipitate. Thus, ordinary compact bone, unlike the other connective tissues, contains no mucin, and from this it appears that in the process of ossification the connective tissue matrix is completely calcified. W. D. H.

Lacto-globulin. By R. T. Hewlett (*J. Physiol.*, **13**, 798—802).—Sebelien stated that ordinary cows' milk contains a small quantity of globulin (precipitable by saturation with magnesium sulphate after the caseïnogen has been precipitated by saturation with sodium chloride).

Halliburton (Abstr., 1891, 339) found that this precipitate does occur, but considered it to be a portion of the lactalbumin precipitated by the saturation with two salts.

Sebelien (Abstr., 1991, 951) having reaffirmed his original statements, the present research was undertaken to test their accuracy. The following conclusions are arrived at:—

1. Sodium chloride is a more perfect precipitant of caseïnogen than magnesium sulphate.

2. Caseïnogen in milk is not completely precipitated by saturation with either sodium chloride or magnesium sulphate, a small quantity

remaining in solution, and this is precipitable by warming to 35°, or by saturation with a second neutral salt.

3. This residual caseïnogen is, possibly, more intimately associated with the calcium salts in milk than the rest of the caseïnogen, as the precipitate is found to be mixed with a considerable quantity of calcium sulphate; this is more abundant when the milk is first saturated with magnesium sulphate, and then with sodium chloride.

4. This residual caseïnogen forms the greater part of Sebelien's lacto-globulin; there is, however, a very small quantity of a true globulin present; it is precipitated by dialysis, and by saturation with neutral salts, coagulable by heat, and not by rennet.

5. In order to prepare pure lacto-albumin, it is necessary to dialyse its solution for some time to precipitate remaining traces of caseïnogen and globulin. **W. D. H.**

Microchemical Localisation of Phosphorus in the Tissues. By L. LILIENFELD and A. MONTI (*Zeit. physiol. Chem.*, **17**, 410—424).—The importance of phosphorus in bio-chemistry is very great: for not only inorganic phosphates occur, but organic compounds like lecithin, protagon, and nucleïn.

The method recommended for detecting this element, microchemically, in the tissues is the following:—

The organ or tissue must be fresh; the preparation is placed in a solution of ammonium molybdate, and is left there for minutes or hours, according as to whether the phosphorus is in a simple or complex union. The pieces of tissue, which appear yellow to the eye if much phosphorus is present, are then washed with water containing a little pyrogallol, until the liquid no longer takes a brown-yellow tint, but remains clear. The pieces are then placed in 20 per cent. pyrogallol; this reduces the phosphomolybdic acid, and leads to yellow, brown, or black coloration, according to the amount of phosphorus present. After a few minutes, the preparation is again washed, and examined microscopically in water, or it may be passed through alcohol into xylene, and mounted in balsam.

For sections, the following modification is recommended:—The sections are taken directly from the molybdate to an ethereal solution of pyrogallol. The coloration is not so diffused as when water is used in washing.

The method was found to give good results with substances like nucleïc acid rich in phosphorus, whilst it gave negative results with proteïds free from phosphorus. It was then applied to cells and tissues with the following results:—

1. Cells in general. The nucleus is deeply coloured, especially the karyomicrosomes, and the optical sections of the nuclear network. The protoplasm is coloured also, but less intensely. In cell division, it is the chromatic fibres which are most stained. This, however, was in vegetable cells. In the cells of the testis, the protoplasm is so rich in phosphorus that hardly any distinction between it and the nucleus could be made out. The cell membrane of plant cells is not coloured; the crystals of plant vitellin are deeply coloured.

2. Bacteria are coloured a weak brown.

3. Epithelial cells of the frog and salamander's epidermis.—The nucleus is coloured; in the deeper layers the cytoplasm is coloured also, but less deeply; on the surface, when mucin is being formed, it is not coloured.

4. Hydra.—Here also the nuclei are better stained than the protoplasm.

5. Spermatozoa.—The head is intensely coloured; the rest not. In dog's spermatozoa the hinder part of the head is most coloured.

6. Blood.—The red corpuscles are stained a deep yellow-brown, due probably to lecithin. The leucocytes behave like other cells; their nucleus is darkly, their cytoplasm faintly, coloured. The platelets are dark brown.

7. Connective tissues.—Here the nuclei of the cells stand out prominently.

8. Bone.—The large amount of phosphates here rendered the observations valueless.

9. Cartilage.—The matrix is free from phosphorus; the cells contain it, especially their nuclei.

10. Nerve cells.—Here the nuclei are less coloured than the cytoplasm.

11. Kidneys.—The whole cytoplasm is rich in phosphorus; this is probably due to phosphates passing into the urine.

12. Muscle.—The deep colour readily produced here is also probably due to phosphates. The coloration is most marked in the dark stripes.

W. D. H.

Lactic acid in Blood and Urine. By T. Irisawa (*Zeit. physiol. Chem.*, **17**, 340—352).—The results of this research may be summed up as follows:—

1. Lactic acid is always present in blood removed from the dead body.

2. In urine drawn off from men shortly before death, lactic acid was found three times in seven cases.

3. The presence of lactic acid in blood corpuscles and pus was also noted.

4. In blood drawn freshly from the veins of a dog, lactic acid was found in each experiment.

5. In artificially produced anæmia, the amount of lactic acid in the blood rises in proportion to the lessening of oxidation processes.

Crystals of potassium dihydrogen phosphate were prepared from liver and pancreas; the acidity of dead organs is probably partly explicable in this way.

W. D. H.

Action of Phosphorus and of Arsenious Anhydride on the Animal Organism. By T. Araki (*Zeit physiol. Chem.*, **17**, 311—339).—In previous researches (Abstr., 1891, 1125, 1392; 1892, 517, 1113) it has been shown that various circumstances tending to a diminution of oxidation processes in the body lead to the appearance of lactic acid in the urine; the present communication is a continuation of these, the experiments being performed on dogs and rabbits. The phosphorus was administered dissolved in olive oil, subcutaneously;

the arsenious anhydride was mixed with the food. In the case of phosphorus poisoning, lactic acid appears quickly after the poison is given; the amount varies, and the variations show no relation to the liver affection produced. The amount of lactic acid in the urine may be increased by combining carbonic oxide poisoning with that produced by phosphorus. Jaundice sets in later; it is almost entirely bile pigment only that passes into the urine.

The appearance of lactic acid in the urine cannot be explained on the grounds of anæmia. The amount of blood pigment varies but little. It is probably due to the diminished activity of the heart, and thus indirectly to a lessening of oxidation processes by the slowing of the circulation through the lungs and tissues.

Glucose is seldom formed in the urine, thus contrasting with carbonic oxide poisoning. Leucine and tyrosine were never found.

The action of arsenious acid is precisely similar, only rather slower in onset. W. D. H.

Putrefaction in the Intestines. By C. Schmitz (*Zeit. physiol. Chem.*, **17**, 401—403).—Rovighi (Abstr., 1892, 226), Winternitz (*ibid.*, 1116), and others have stated that a diet of milk or kephir lessens the ethereal hydrogen sulphates in the urine. This has been ascribed to the lactic acid produced from the milk sugar acting as an antiseptic in the intestines.

The present communication states:—

1. That feeding with lactose, mixed with the ordinary diet, causes no lessening of the output of ethereal hydrogen sulphates.

2. Administration of free hydrochloric acid with the food causes, in dogs, no lessening of the ethereal hydrogen sulphates in the urine.

3. In man, however, 40 or 50 drops of a 10 per cent. solution of hydrochloric acid, given in the day, lessen the output of these sulphates by as much as 40 per cent. This is in accordance with the observations of Biernacki (*Deut. Arch. klin. Med.*, **49**, Heft 1).

4. The constituent of milk and kephir, which produces the lessening in the output of these sulphates is caseïn. Feeding dogs on freshly precipitated caseïn produces this result. W. D. H.

Ptomaïnes from the Urine in Erysipelas and Puerperal Fever. By A. B. Griffiths (*Compt. rend.*, **115**, 667—669).—See this vol., i, 183.

Chemistry of Vegetable Physiology and Agriculture.

Interchange of Carbonic Anhyride and Oxygen between Plants and the Atmosphere. By T. Schloesing, Jun. (*Compt. rend.*, **115**, 881—883).—The plants were grown in sealed vessels in a soil of quartz sand mixed with a little chalk, and were watered with

fertilising solution. The uppermost layer of the soil was ignited to prevent the growth of algæ, but even then a blank experiment showed that a slight amount of carbonic anhydride was absorbed, and oxygen evolved.

After the seeds were sown, the air was exhausted from the vessel and replaced by known quantities of pure nitrogen and oxygen, and during the growth, the composition of this atmosphere, small samples of which were withdrawn and analysed from time to time, was adjusted by adding known quantities of carbonic anhydride, or removing known quantities of oxygen by circulation over a known weight of red-hot copper. The total volume of the gas was again measured at the end of the experiment.

Plants of large-leaved cress from 0·0437 gram of seed absorbed in 47 days from the sowing at the end of April, 1171·5 c.c. of carbonic anhydride, and gave out 1563·4 c.c. of oxygen, or in the ratio of 0·75 : 1. Plants of feather-grass (*houque laineuse*) from 0·05 gram of seed absorbed in 43 days, 1501 c.c. of carbonic anhydride, and gave out 1836 c.c. of oxygen, or in the ratio of 0·82 : 1. Jn. W.

Absorption of Free Nitrogen by Plants. By T. Schloesing, Jun., and E. Laurent (*Compt. rend.*, **115**, 732—735; Duclaux, *ibid.*, 735—736; and Berthelot, *ibid.*, 737—738).—Schloesing and Laurent have investigated, by the methods previously described, the absorption of free nitrogen by soils on which are growing various algæ, the precise nature of the algæ being determined by Bornet. With cultivations of *Nostoc punctiforme*, *N. minutum*, *Brachythechium rutabulum*, and *Barbula muralis*, in some cases separate, in others mixed in pairs, the absorption of atmospheric nitrogen was very distinct, but no such absorption was observed with cultivations of the similar alga *Microcoleus vaginatus*. Estimation of the carbon and nitrogen in the superficial layer of the soil indicates that the nitrogen absorbed is found in the tissues of the plants, the energy required being provided through the medium of the chlorophyll.

It follows that the absorption of atmospheric nitrogen is effected by the lower vegetable organisms at the surface of the soil, and not, as Berthelot supposes, through the influence of microbes in the body of the soil

Duclaux, at whose suggestion Schloesing and Laurent undertook these investigations, points out that the occurrence of algæ and lower organisms at the surface of the soil had frequently been observed by Berthelot and others, but that their true function had been overlooked.

Berthelot points out that in one of his earlier papers he showed that the absorption takes place both at the surface of the soil and throughout the mass, and he contends that, although Schloesing and Laurent have proved that certain algæ and other lower organisms containing chlorophyll have the power of absorbing free nitrogen, they have advanced no evidence that this power is not also shared by colourless lower organisms which seem to contain no chlorophyll (as in his own experiments with humic acid) and which occur below the surface of the soil. C. H. B.

Colouring Matter of Pollen. By G. Bertrand and G. Poirault (*Compt. rend.*, **115**, 828—830).—Yellow and orange pollen from various flowers, with the exception of dry pollen, such as that of *Urticæ*, *Gramineæ*, and the like, contain carotene, which can be extracted with light petroleum, and is identical with the carotene from other sources. Colorimetric estimation indicates that the oily drops on the surface of the pollen of *Verbascum thapsiforme* contain not less than 6·6 per cent. of carotene, which is a relatively high proportion. The carotene occurs in the oily drops that cover the surface of the pollen grains, and it is not improbable that the odour of the product of the spontaneous oxidation of the carotene is attractive to insects.

C. H. B.

Carbohydrates in Leguminous Seeds. By E. Schulze (*Landw. Versuchs-Stat.*, **41**, 207—229).—It is probable that β-galactan is present in the seeds of *Pisum sativum*, *Vicia sativa*, and *V. faba*, and that paragalactan occurs in *Pisum sativum*, *Vicia faba*, and in *Soja hispida*, although both have hitherto been prepared from the seeds of *Lupinus luteus*.

β-Galactan (lupeose, Abstr., 1892, 1171) gives no precipitate with sodium, ammonium, and magnesium sulphates, and with ammonium phosphate, and is therefore, perhaps, not a colloïd substance (compare G. Pohl, *Zeit. physiol. Chem.*, **14**, 154). On the other hand, all attempts to obtain it in a crystalline form failed. In this respect, it differs from stachyose, as well as in its behaviour towards strontium hydroxide which precipitates β-galactan and towards hot dilute sulphuric acid. Whilst stachyose yields galactose, grape sugar, and fruit sugar, β-galactan yields galactose, fruit sugar, and at least one other glucose, but no grape sugar. The formula of β-galactan is probably $C_{24}H_{44}O_{22}$ or $C_{36}H_{60}O_{33}$. The amount of β-galactan in lupin seeds was estimated (*Landw. Versuchs-Stat.*, **39**, 283) by boiling an aqueous extract with dilute hydrochloric acid, extracting the glucose, and calculating the amount of β-galactan, on the assumption that 100 parts of β-galactan yield 111 parts of glucose: a percentage of 10·20 was found. Inasmuch as fruit sugar is also found, it is obvious that the result was too low; in fact only about 80 per cent. of the theoretical amount of glucose is actually produced. The percentage of β-galactan would thus be 12·75 (instead of 10·20). Almost the same results (13·12 and 12·44) were obtained with other samples of seeds by comparing the results obtained from the aqueous extracts with that obtained with β-galactan itself. Another determination by means of the amount of mucic acid obtained by oxidation with nitric acid, gave the percentage 11·2. The results indicate that β-galactan is the only soluble carbohydrate which occurs in lupin seeds in any quantity.

When paragalactan is hydrolysed, arabinose is formed as well as galactose, and it is suggested that the name of paragalactan should be altered to *paragalactoaraban*. It was already shown (*Landw. Versuchs-Stat.*, **36**, 447) that this substance is very easily altered by acids, and it seemed desirable to examine the behaviour of the substance towards Hoffmeister's reagents for cellulose (*Landw. Jahrb.*, **17**, 239). For this purpose, the residue obtained by extracting finely-

powdered lupin seeds with ether, then with dilute aqueous potash, and finally with water, was employed. This residue contained crude protein (3·38), non-nitrogenous substance (85·72), and ash (10·90 per cent.). When treated successively with a mixture of hydrochloric acid and potassium chlorate, and with hot, dilute ammonia, an average amount of 25·71 per cent. of cellulose was obtained (30 per cent. of the non-nitrogeneous constituents of the residue). Glacial acetic acid at 90° (Hoffmeister's method for removing starch, *Landw. Jahrb.*, **18**, 774) dissolves the greater part of the residue, which is thus scarcely more stable than starch (compare Abstr., 1890, 284).

N. H. M.

Amount of Ash in Etiolated Leaves. By W. PALLADIN (*Expt. Stat. Record*, **4**, 207; from *Ber. deut. bot. Ges.*, 1892, 179).—Etiolated leaves of wheat and vetch were found to contain less ash than the green leaves; the difference was specially marked in the case of the calcium. A similar diminution of ash was observed with plants grown in air kept saturated with moisture, that is, with hindered transpiration. This, in conjunction with the fact that the conditions of etiolation hindered transpiration, indicates a connection between transpiration and the acquisition of ash constituents.

N. H. M.

Analyses of California Prunes, Apricots, and Peaches. By G. E. COLBY and H. P. DYER (*Exp. Stat. Record*, **4**, 157—162; from *Californ. Bul.*, No. 97, 1892).—The following analytical results, obtained with the various fruits, are given:—

	In fresh fruit (per cent.).				In juice (per cent.).	
	Dry matter.	Ash.	Nitrogen.	Sugar.	Sugar.	Acid (as SO_3).
Peaches (1)	21·50	0·62	—	15·00	20·00	0·17
Peaches (2)	13·50	0·44	—	10·00	14·00	0·32
Prunes	18·71	0·40	0·148	11·65	16·70	0·43
Apricots	14·43	0·52	0·229	10·76	13·34	0·63
Dried prunes	72·00	1·65	—	47·25	—	0·62

The percentage composition of the pure ash of the whole fruit of (i) French prunes and (ii) Royal apricots is next given.

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	MnO_2.	P_2O_5.	SO_3.	SiO_2.	Cl.
I.	65·92	3·18	3·24	6·16	0·85	0·31	15·19	2·37	4·56	0·19
II.	54·88	10·57	3·52	3·85	1·71	0·31	13·86	2·95	7·85	0·60

After grapes, apricots remove most mineral matter from the soil; prunes and oranges taking, about equally, the third place. This is contrary to results obtained with European fruits. A table is given showing the amounts of ash, potash, phosphoric acid, and nitrogen in 1000 lbs. of the European and Californian fruits. Whilst Californian

prunes withdraw less mineral, they take up more nitrogen than the European. With regard to apricots, the Californian and European contain about the same amounts of mineral matter, but the former take 2·5 times as much nitrogen as the latter. N. H. M.

Relative Value of Maize Silage and Field and Fodder Maize for Milk and Butter Production. By L. W. Woll (*Exp. Stat. Record.*, **4**, 187—180; from *Wiscon. Stat. Rep.*, 1891, 49—60).—Twenty cows were divided into two lots, which were fed alternately on silage and fodder *ad libitum* in conjunction with hay (4 lbs.), wheat bran (5 lbs.), and wheat shorts (2 lbs.). The first period of the experiment was from December 15 to February 9; the second, February 16 to April 13; each being preceded by a week of preliminary feeding. The weight of milk was recorded each milking, and every three or four weeks the morning and evening milk of each cow was tested by the Babcock method for a week. At such times the cows were weighed daily, and the amount of water consumed ascertained. The total food consumed at each feeding and the amounts left over were recorded. During the silage period, it was found that the average weight of cows was greater than when fed with fodder. The total amounts of milk produced with silage and fodder maize were almost identical, but when the areas of land required to produce the two foods are considered, it is seen that silage would have produced 243 lbs. more milk (or 12 lbs. of butter) than the dry fodder, equivalent to a gain of a little more than 3 per cent. in favour of the silage. N. H. M.

Losses in ensiling and field-curing Maize. By F. W. Woll (*Exp. Stat. Record*, **4**, 145—147; from *Wiscon. Stat. Rep.*, 1891, 227—231).—129,014 lbs. of maize was put into a silo with 3800 lbs. of millet as a covering. The silage was good with the exception of the top 6 inches. The same weight of maize was left in the field for the greater part of the winter, which was favourable, although the autumn was wet. The maize contained in each case 32,432 lbs. of dry matter and 2580·5 lbs. of proteïn. Of this the silage lost 10·3 per cent. of dry matter and 12·5 per cent. of proteïn; whilst the field-cured maize lost 28·3 per cent. of dry matter and 34·8 per cent. of proteïn. In previous years, the loss in the ensilage was greater, which was probably due to the small quantity of fodder employed. N. H. M.

Influence of the Distribution of Manures in the Soil on their Utilisation. By T. Schloesing (*Compt. rend.*, **115**, 698—703 and 768—771).—A poor soil prepared by mixing 84 parts of a very sandy subsoil with 16 parts of an argillaceous subsoil was mixed with potassium sulphate, sodium nitrate, superphosphate from bones, and magnesium sulphate. In the first case, the manures were dissolved in water and every care was taken to mix them as uniformly with the soil as possible. In the second case, the soil, which measured 1·75 m. in length, 1·2 m. in breadth, and 0·35 m. in thickness, was cut into eight longitudinal furrows, 12 cm. deep and 15 cm. apart, and one eighth of the mixed manure was spread along the bottom of each

furrow, the furrows being afterwards filled up. In both cases the soil was previously mixed with about 0·25 per cent. of chopped straw in place of humus.

Each quantity of soil was divided into five sections, and wheat, potatoes, beet, haricots, and peas were sown on separate sections. The experiments with beet gave no results in consequence of the attacks of insects and fungi. Wheat, potatoes, haricots, and peas developed somewhat more vigorously in the second case, where the distribution of the manure was irregular, but reached maturity somewhat later, the differences in the time of ripening being least in the case of wheat.

Wheat, haricots, and potatoes gave a distinctly larger crop with an irregular than with a uniform distribution of manure, whilst peas gave practically the same weight of crop under both conditions. The first three plants also utilised a distinctly larger proportion of phosphoric acid when the manure was irregularly distributed, whereas with peas the reverse was the case, probably because the plant developed before the phosphoric acid had time to diffuse through the soil. All four crops utilised a markedly higher proportion of nitrogen when the distribution was irregular, and haricots, peas, and potatoes utilised a considerably higher proportion of potassium. Wheat utilised a somewhat lower proportion of potassium when the distribution was irregular. If the crops in the second case (irregular distribution) had been allowed to ripen fully instead of being cut when the crops in the first case (uniform distribution) were ready, the differences would have been still greater in favour of the second case.

It would seem that, so far as these experiments go, the manures experimented with are better utilised by crops when distributed in lines than when uniformly diffused through the soil. In the former case, a certain number only of the rootlets come in contact with the manure, but meet with it in a concentrated form, whereas in the latter all the rootlets are alike in contact with the manure but the manure is, so to speak, in a much more diluted form. C. H. B.

Employment of Ferrous Sulphate in Agriculture. By H. Boiret and G. Paturel (*Ann. Agron.*, **18**, 418—440).—After remarking on the conflicting nature of the evidence as to the benefit or injury to crops to be derived from dressings of ferrous sulphate, the authors give a historical sketch of our knowledge on the question and follow this by detailed accounts of recent experiments executed by themselves at Grignon.

Pyritous shales have been long employed in the districts in which they are found. As at first extracted they contain, according to Lefebvre's analysis: iron sulphide, 19·4; carbonaceous matter, 22·5; clay, 34·0; calcium sulphate, 1·9; water, 22·2. Nitrogen is present to the extent of 0·5 to 1·0 per cent. These shales are used as manures after 15—18 months exposure to air, when most of the sulphide is transformed into iron and aluminium sulphates. An instance is given, from experiments made in 1777, where a small dressing of this material (about 850 litres per hectare) more than doubled the

yield of sainfoin as compared with an unmanured plot, aad produced a greater increase than a good dressing of farmyard manure. The nitrogen in this dressing would be insignificant; leguminous crops show the greatest benefit from this application. Sir H. Davy's opinion, in commenting on the results obtained with ferrous sulphate by Pearson, was that this substance acted by producing gypsum, and on the same theory he explained its injurious action when lime is lacking in the soil. Gris and Dumont, in France, and Griffiths, in England, have since noticed the deepening of the green tint in chlorotic plants after a very small dressing of ferrous sulphate, and Griffiths has obtained some remarkable increases of crop by employing the salt at the rate of $\frac{1}{2}$ cwt. per acre, in the case of beans, turnips, potatoes, hay, and mangolds, but not with cereals. He maintains that the dressing greatly increases the proportion of iron and of phosphoric acid in the ash of the crops, but diminishes the potash. The author's experiments were as follows:—

Action of Solutions of Ferrous Sulphate on Plants.—Seedlings of peas and oats were supported with their roots immersed in solutions of ferrous sulphate and other salts of known strengths. After a month of immersion in pure water and in sodium nitrate, ammonium sulphate, sodium chloride, or magnesium sulphate solution (2:1000), the plants were healthy and growing; less healthy in the same saline solutions at 5:1000. In ferrous sulphate, lead acetate, copper sulphate, or zinc sulphate, of either strength they were absolutely dead. Experiments with more dilute solutions of ferrous sulphate showed that whilst dilutions of 1/1000 and 1/2000 were still very injurious, a certain amount of growth was possible in dilutions of 1/4000, especially where some of the iron was deposited by oxidation as basic ferric sulphate. During this oxidation free sulphuric acid is formed, which is very deleterious to plants, solutions of 1/5000 being fatal; but in an extremely dilute solution it may be neutralised by calcareous dust from the air. In every case where the solutions of ferrous sulphate became perceptibly acid by oxidation, the plants were killed or injured. Solutions of iron citrate and citric acid are as injurious as those of iron sulphate and sulphuric acid.

Cultures in Artificial Soils containing known proportions of Calcium Carbonate.—The general result of these experiments is that ferrous sulphate is always injurious if the soil does not contain an excess of lime. Directly the drainage water shows traces of free acid, or of soluble iron compounds, injury is perceived. Should these soluble compounds get washed down into a lower stratum of soil, plants will grow in the surface soil, but their roots will not penetrate the lower layer at all. Should the soil contain much lime, large dressings of ferrous sulphate may be applied without injury, especially if this be done some time before crops are sown. A dressing at the extreme rate of 20 kilos. per square metre incorporated with a soil containing 19 per cent. of calcium carbonate was more of less injurious to peas and oats sown the same day; many of the plants failed, but those of the oats which grew were not inferior to those grown in plain soil. After removing the peas and oats, white mustard was sown on the same plots and flourished normally; at this

date no free acid or soluble iron salt could be detected in the soil at any depth. Determinations of total solids, ash, phosphoric acid, potash, and iron in the peas and oats grown with or without a heavy dressing of ferrous sulphate exhibited no differences which could be traced to the influence of this salt. The conclusions of Griffiths on this point are in contradiction with those of the authors.

To sum up, they consider ferrous sulphate beneficial only where the soil contains an excess of lime; its direct effect is to produce gypsum, to which much of the benefit must be ascribed, although there may be secondary benefits; the proportion of phosphoric acid in the crops raised with ferrous sulphate is not increased, nor is that of potash decreased, as was the case in Griffith's experiments.

J. M. H. M.

Analytical Chemistry.

Potassium Hydrogen Tartrate in Volumetric Analysis. By A. BORNTRAEGER (*Zeit. angw. Chem.*, 1892, 294).—The author, some time ago, proposed to use potassium hydrogen tartrate for the standardising of volumetric alkali. He now points out that the salt may be conveniently used to prepare normal alkali without the use of a normal acid. To prepare normal soda, an approximately prepared solution of sodium hydroxide, which must be free from carbonic acid, is added to a hot solution of 3·7626 gram of potassium hydrogen tartrate, until the liquid is neutral. If less than 20 c.c. of the alkali is required, the soda must be proportionally diluted. L. DE K.

Gas-volumetric Estimation of Iodine. By L. MARCHLEWSKI (*Zeit. angw. Chem.*, 1892, 205—206).—The author, who at first did not get satisfactory results with Baumann's gas-volumetric method, has now, however, been very successful when following Baumann's latest directions (compare this vol. ii, 87). L. DE K.

Estimation of Nitrogen by Kjeldahl's Method. By O. BÖTTCHER (*Landw. Versuchs-Stat.*, **41**, 170—173).—In estimating nitrogen in substances free from nitrates, Wilfarth's modification of Kjeldahl's method was found to be the most suitable. Copper sulphate was employed for a long time, until it was found that with substances which are difficult to decompose, such as horn meal, fish meal, &c., considerably more nitrogen was found when mercury was used than with copper sulphate, although the boiling with copper sulphate was continued as long as possible (4—5 hours), and the liquid was colourless when cold. With mercury, two hours' boiling is sufficient; and it was found unnecessary to add potassium sulphide and zinc before distilling, 1·5 gram of zinc dust being sufficient. In view of the many essential alterations made from time to time in the Kjeldahl method, Stutzer has proposed to substitute the name "sulphate method."

N. H. M.

Estimation of Nitric Nitrogen. By O. Böttcher (*Landw. Versuchs-Stat.*, **41**, 165—169).—The following method was found to give very good results, both with Chili saltpetre and with the most various mixed manures:—The saltpetre (10 grams) is dissolved in water (500 c.c.), and of this solution, 25 c.c. put into a 400 c.c. distilling flask with water (about 120 c.c.), washed and dried zinc dust (5 grams), powdered iron (5 grams), and aqueous soda (80 c.c. of 32° R.). The flask is then connected with a condenser provided with a receiver, containing 20 c.c. of titrated sulphuric acid, and after one or two hours, 100 c.c. is distilled off, and titrated as usual. A number of analyses made by the method are given.

N. H. M.

Modified Gunning-Kjeldahl Method for use in presence of Nitrates. By A. L. Winton (*Chem. News*, **66**, 227—228).—The following modification of the Gunning-Kjeldahl method is suggested to render it available in the presence of nitrates. 0·5 or 1 gram is digested for two hours, with 80 c.c. of a mixture containing 2 grams of salicylic acid for every 30 c.c. of sulphuric acid, the mixture being frequently agitated, 2 grams of zinc dust is then added, shaking continuously, and after heating the flask gently, until dense fumes cease to be evolved, 10 to 12 grams of potassium sulphate is added, the boiling being continued to complete oxidation. Water is carefully added to and shaken with the mixture, as the latter commences to solidify on cooling; the subsequent distillation with soda is conducted in the usual manner.

D. A. L.

Microchemical Localisation of Phosphorus in the Tissues. By L. Lilienfeld and A. Monti (*Zeit. physiol. Chem.*, **17**, 410—424). —See this vol. ii, 135.

Gravimetric Estimation of Sulphuric Acid. By M. Weinig (*Zeit. angw. Chem.*, 1892, 204—205).—The author recommends the following process:—An accurately measured quantity of the acid is introduced into a weighed platinum dish, and mixed with a very small excess of ammonia. The solution is evaporated to dryness, and the residue is finally dried for half-an-hour at 115—120°. After cooling in a desiccator, the whole is weighed. The sulphuric acid is then calculated from the amount of ammonium sulphate thus obtained. The results are said to be more accurate than those obtained by precipitation with barium chloride.

L. de K.

The Action of Benzoic Chloride on Ammonia. By V. Lehmann (*Zeit. physiol. Chem.*, **17**, 404—409).—Benzoic chloride is a reagent much used for the separation of diamines and other substances from urine.

When shaken with ammonia, benzamide is formed. The benzamide can be obtained by repeated shaking of the aqueous solution with ether. This may cause a small error in those analyses of urine in which benzoic chloride is used. The reagent does not act, however, on urea, or on creatinine.

W. D. H.

Estimation of Urea. By E. Bödtker (*Zeit. physiol. Chem.*, **17**, 140—147).—The best method of estimating urea is found to be that of Sjöqvist and Mörner (Abstr., 1891, 146). W. D. H.

Volumetric Estimation of Alkaloïds. By L. Barthe (*Compt. rend.*, **115**, 512—514).—All the well-known vegetable alkaloïds are alkaline to litmus, but are neutral to phenolphthaleïn. It follows that if a solution containing an alkaloïd is titrated with sodium or potassium hydroxide, using litmus as an indicator, the alkali used will correspond with the quantity of free acid in the liquid, but if phenolphthaleïn is the indicator, the quantity of alkali used will correspond with the sum of the acid present in the free state and the acid present in combination with the alkaloïd. The difference between the two titrations gives the quantity of acid in combination with the alkaloïd.

The quantity of alkaloïd taken should be about 0·001 of a gram-equivalent, and should be dissolved in 10 or 20 c.c. of decinormal acid and mixed with 20 c.c. of alcohol of 90°. For the titration with litmus the alcohol should be omitted.

The method is not applicable in the case of atropine or narcotine, but the results are not affected by the presence of salts of the alkalis or alkaline earths, or of salts of certain metals such as zinc.

It is obvious that in the case of crystallised salts, the method is applicable to the determination of water of crystallisation, since titration with litmus as indicator then gives the quantity of combined acid, and titration with phenolphthaleïn gives the quantity of alkaloïd. C. H. B.

Estimation of the Nitrogenous Constituents of Commercial Peptone. By A. Stutzer (*Zeit. anal. Chem.*, **31**, 501—515).—The value of commercial peptones depends essentially on the amount of albumose and peptone they contain. Gelatin and gelatin-peptone, leucine, tyrosine, and other decomposition products are comparatively valueless. The following process is directed to the estimation of these constituents:—In all cases, the amount of any precipitate is not found by weighing, but is calculated from the result of a nitrogen estimation by Kjeldahl's process, on the assumption that they all contain 16 per cent. Of dry preparations 5 grams is taken; of fluids, 20—25 grams. This is warmed with 200 c.c. of water, feebly acidified with acetic acid, boiled, and filtered, the filtrate being made up to 500 c.c. The filter, with the moist precipitate, is at once submitted to Kjeldahl's process, and a correction is made for the nitrogen in the paper. This gives the amount of unchanged albuminous substances. In a well made preparation these should not be present. The nitrogen in the filtrate is also determined, and the sum of the two stated as total nitrogen. A fresh portion of substance, dissolved in 25 c.c. of water (or, if a liquid, 50 c.c. concentrated to 25 c.c.), is gradually mixed with 250 c.c. of absolute alcohol, and filtered after 12 hours. The filtrate, which contains the gelatin-peptone, the leucine, tyrosine, and other decomposition products, is freed from alcohol and dissolved in water. Any insoluble matter is filtered off, and regarded as albumose. The clear solution is made up to 500 c.c., and 100 c.c. of this, warmed

to about 40°, is precipitated with 10—15 c.c. of a paste of mercuric oxide, containing about 15 per cent., and prepared by pouring mercuric chloride into dilute soda, washing thoroughly, and preserving in the dark. After stirring for a few minutes, the mixture is filtered and the nitrogen determined in the precipitate and filtrate. The former contains the gelatin-peptone, with unknown decomposition products of albumose and peptone. The filtrate contains the leucine, tyrosine, and other products of a digestive fermentation which has been carried to excess, together with part of the so-called flesh bases (creatine, &c.), which are very sparingly soluble in 95 per cent. alcohol. Instead of mercuric oxide, phosphotungstic acid may be used. This reagent, used in excess, precipitates none of the flesh bases except xanthine and hypoxanthine, of which, from their sparing solubility, only traces can be present in the alcoholic solution.

The alcohol precipitate containing the albumose, gelatin, and peptone is rinsed with water into a beaker and warmed until the alcohol is expelled. Any albumose which has been rendered insoluble is filtered off and washed with hot water. The clear solution is made up to 500 c.c., and of this, 50 c.c., mixed cold with an equal volume of dilute sulphuric acid (1 vol. to 3 vols. of water), is completely precipitated with phosphotungstic acid. The nitrogen in the precipitate gives the joint amount of the albumose, peptone, and gelatin. 100 c.c. of the same solution, concentrated on the water-bath to 8—10 c.c., is mixed with 100 c.c. of a cold saturated solution of ammonium sulphate. The precipitate is collected and washed with a saturated solution of ammonium sulphate. It is then dissolved in tepid water, and whilst one portion of the solution is used for nitrogen estimation, another is precipitated by barium chloride, to ascertain the amount of adhering ammonium sulphate. (The relation of the ammonia to the sulphuric acid in the solution used should be determined, not calculated.) The corrected nitrogen in the precipitate gives the amount of albumose and gelatin. The peptone is known by difference, its actual presence being confirmed by concentrating the remainder of the solution, precipitating the albumose and gelatin by solid ammonium sulphate, and testing the filtrate by addding a trace of cupric sulphate and a large excess of strong soda solution. Peptone gives a characteristic red colour.

The gelatin is best estimated by means of the viscosimeter, the viscosity being compared with that of a standard solution of the best white gelatin, to which an equal volume of a 20 per cent. solution of serum peptone, free from gelatin, has been added. A 10 per cent. solution of the substance is prepared and cooled for three hours to a temperature lower than that at which the comparison is to be made. It is then gradually warmed to a standard temperature, and immediately examined for viscosity. Very dilute solutions may be compared at 0—1°, whilst strong ones may need to be warmed to 25°, but it is not permissible to warm above the standard temperature, and again cool just before testing. Calling the viscosity of a 10 per cent. solution of serum peptone 100, the addition of 0·25 per cent. of gelatin raises it to 130 at 0—1°, 114 at 15°, 106 at 20°.

Having now ascertained the amount of nitrogen in the alcohol

precipitate in the form of albumose, peptone, and gelatin, the remaining nitrogen is to be regarded as belonging to the flesh bases. The principal of these is creatine, with 32·8 per cent. of nitrogen, whence the multiplication of the nitrogen by the factor 3·12, gives the total amount of the bases with but small error. M. J. S.

Detection of Resin in the Sizing of Paper. By W. Herzberg (*Chem. Centr.*, 1892, ii, 275; from *Mitt. k. tech. Vers.-Anstalt, Berlin*, **10**, 80—85).—A piece of the paper to be examined is placed on a support and over a hole in the latter, so that the paper can be seen by transmitted light; 4—6 drops of ether are then allowed to fall on it.

If the paper has been sized with resin, a bright, translucent ring of resin is left after the ether has evaporated; if a mixture of resin with gelatin has been used, a repetition of the treatment may be necessary in order to obtain the ring. Paper sized with gelatin only leaves no such ring. C. F. B.

Analysis of Sealing Wax. By C. Mangold (*Zeit. angw. Chem.*, 1892, 75—76).—Five grams of the powdered sample is boiled in a 250 c.c. flask with 150 c.c. of alcohol on a water-bath. After cooling, alcohol is added to the mark, and after thorough mixing and settling, 50 c.c. is pipetted off and mixed with an excess of Hübl's reagent. The portion insoluble in alcohol is filtered through a tared filter, dried at 110°, and weighed. It generally consists of chalk or magnesia, plaster of Paris, zinc-white, barytes, or even china clay, or tripoli. The colouring is, in the best brands, vermillion; in the inferior red ones, it generally consists of red oxide of iron, or red lead, whilst the black samples are mostly coloured with bone-black.

It is assumed by the author that the turpentine used in the manufacture of sealing wax has changed into colophony. Disregarding the mineral matter, sealing wax may, therefore, be taken to be a mixture of colophony and shellac. As there is an enormous difference between the iodine absorptions of colophony (115) and shellac (6), the iodine number of the sample affords ready means for the calculation of their respective percentages. L. de K.

Testing Linseed Oil Varnish. By W. Fahrion (*Zeit. angw. Chem.*, 1892, 171—173).—The author has found that linseed oil, on boiling and subsequent exposure, rapidly loses its power of absorbing iodine from Hübl's solution. The iodine numbers of three samples of boiled linseed oil, derived from the same original raw oil, had decreased respectively to 101·3, 77·3, and 73·7. The same effect is noticed on warming cotton-seed oil, which, instead of absorbing 108 per cent. of iodine, will then only take up about 70 per cent. The decrease in iodine absorbing power is, according to the author, not so much due to oxidation as to polymerisation.

With this decrease there is, however, a large increase in the amount of oxy-acids, which should, therefore, be estimated in every sample supposed to be stale (compare this vol., ii, 56). L. de K.

General and Physical Chemistry.

Absorption Spectra of Copper Salts in Aqueous Solution. By T. Ewan (*Phil. Mag.* [5], **33**, 317—342).—The author has examined the absorption spectra of solutions of copper nitrate, chloride, and sulphate, employing Vierordt's method and a universal spectrophotometer by Krüss. The following is a summary of the results arrived at :—

1. The absorption spectra of the three salts examined undergo changes on diluting their solutions.

2. These changes are of such a nature that the spectra tend to become identical in dilute solutions.

3. The behaviour of the salts examined leads to the conclusion that, in strong solutions, the acid and basic parts of the salts are associated in producing absorption of light, whilst, in dilute solutions, they act independently in doing so.

4. These results are in substantial agreement with the hypothesis of electrolytic dissociation.

5. The results cannot be satisfactorily explained on the hypothesis of a hydrolytic dissociation, or on that of molecular aggregates.

J. W.

Difference of Potential at the Contact of mutually reacting Liquids. By J. Brown (*Phil. Mag.* [5], **33**, 532—539).—By a modification of Exner and Tuma's method, in which a water-dropping funnel and two filter-paper cylinders, saturated with the solutions under investigation and connected by a strip of filter paper, were used, the author has determined the difference of potential between the solutions, which were so chosen as to act on each other chemically. A reducing agent becomes positively electrified with respect to an oxidising substance with which it reacts, the difference of potential being, however, very slight. With respect to solutions which enter into double decomposition, there is no clear connection apparent between the observed electromotive forces and the heat equivalents of the reactions, but the concentration of the solutions has an effect.

There is a rough agreement between the heat of dilution of an aqueous solution (or the heat of solution of a pure liquid) and the difference of potential between it and water. The author finds that the rule that "water must show against every electrolytic solution the potential of the faster ion" does not hold good.

J. W.

Electromotive Forces of Gold and of Platinum Cells. By E. F. Herroun (*Phil. Mag.* [5], **33**, 516—520).—A cell was set up consisting of an amalgamated zinc rod immersed in a solution having the composition $ZnCl_2 + 400H_2O$, and of a platinum plate immersed in a solution of sodium platinochloride of the strength $Na_2PtCl_6 + 400H_2O$. The electromotive force of this cell between 12° and 15°

was, when first set up, about 1·7 volts, but afterwards it fell to an average value of 1·525 volts. The value calculated from thermochemical data is 1·548 volts.

A similar cell in which gold and auric chloride take the place of platinum and sodium platinochloride gave a mean electromotive force of 1·844 volts, or 0·2 volt below the calculated value. When a platinum plate was substituted for the gold plate and immersed in the solution of auric chloride, the electromotive force of the cell thus formed was found to be 1·782 volts, that is, less than the gold | auric chloride, but greater than the platinum | platinic chloride combination. Gold has the slightly higher potential when it is immersed along with a plate of platinum in pure water, or in dilute hydrochloric acid. In strong hydrochloric acid, the difference of potential is doubtful, and in nitro-hydrochloric acid, the platinum has the higher potential. J. W.

Electromotive Force of Galvanic Combinations. By W. Hittorf (*Zeit. physikal. Chem.*, **10**, 593—620).—Ammonium nitride, NH_4N_3, is decomposed in aqueous solution by the electric current with evolution of nitrogen at the anode and hydrogen at the cathode in the proportion of three volumes to one. Although the compound decomposes into its elements with considerable development of heat, it requires an electromotive force of more than a volt to effect the electrolytic decomposition.

The author studies various liquid elements with regard to their forces and the relation between these and the thermochemical data of the reactions taking place in the elements. J. W.

Chemistry of the Secondary Battery. By M. Cantor (*Ann. Phys. Chem.* [2], **47**, 424—425).—The author defends his former view that no hydrogen is occluded by the lead cathode in a secondary cell (compare Abstr., 1891, 514) against criticisms offered by Neumann and Streintz (*Ann. Phys. Chem.* [2], **46**, 431). J. W.

Chemical Equilibrium in Mixed Electrolytes. By G. Gore (*Phil. Mag.* [5], **33**, 342—351).—By his voltaic method (compare Abstr., 1892, 930), the author has examined the equilibrium in various mixed electrolytic solutions, and sums up his results as follows:—The mixtures examined were divisible into two classes, namely, those which spontaneously changed with such rapidity that, on mixing, they at once attained a comparatively fixed state of chemical equilibrium, and those which only slowly changed and attained such a state. With mixtures of acids + salts, and of salts + salts, a fixed state of equilibrium was in nearly all cases immediately attained; but with halogens + salts, halogens + acids, and halogens + bases, a greater or less degree of retardation was frequently observed. Doubling the degree of concentration of the solution did not produce any conspicuous effect on the state of equilibrium. Twenty-four hours elapsed before halogens reached a state of comparative equilibrium with the potassium haloïds in solution. The influence of rise of temperature in promoting a rapid attainment of

the final state is very great. When the ingredients of a mixture of halogen and salt (or acid) in water were in equivalent proportions, complete change was accelerated; if the salt or acid was in excess, it was retarded, and excess of halogen had no effect. The addition of caustic alkali to a solution of a halogen considerably retarded the rate of change which occurred on heating, the greatest retardation occurring with chlorine and the least with iodine. J. W.

Conductivity of Electrolytes in various Solvents. By I KABLUKOFF (*J. Russ. Chem. Soc.*, **23**, 391—422).—A solution of hydrogen chloride in various solvents gave the following resistances in ohms:—v is the dilution, that is, the volume in litres in which 1 gram molecule of the acid was dissolved.

Solvent.	v.	Resistance.
Benzene	4·34	12×10^6
Xylene	2·5	72×10^6
Hexane	12·5	48×10^6
Ethyl ether	2·5	14×10^6

The molecular conductivity (μ) of the same substance was found at 25° to be as follows:—

Solvent.	v.	μ.
Water	∞	394·00
Methyl alcohol	97·16	117·06
Ethyl alcohol	100·0	27·16
Propyl alcohol	35·47	9·74
Isobutyl and ethyl alcohols	49·3	10·46
Isobutyl alcohol.....	136·3	4·00
Isoamyl alcohol	25·42	1·25
Ether.....	3·52	0·000039

For acids dissolved in mixtures of alcohol and water, the following relative numbers for the conductivity were obtained, the conductivity of hydrochloric acid being taken as 100:—

$v = 4$

Alcohol per cent.	HCl.	H_2SO_4.	$CCl_3{\cdot}COOH$.	$CH_2Cl{\cdot}COOH$.
10	100	59·64	79·40	8·80
20	,,	61·51	75·70	6·18
30	,,	59·70	68·79	5·02
40	,,	52·38	—	4·47
50	,,	47·66	—	2·87
60	,,	*ca.* 53·77	44·00	2·70
70	,,	61·50	—	1·91
80	,,	53·80	—	1·21

$v = 8$.

Alcohol per cent.	HCl.	H_2SO_4.	$CCl_3 \cdot COOH$.	$CH_2Cl \cdot COOH$.
10	100	59·23	82·99	10·07
30	,,	62·43	79·75	7·08
40	,,	53·55	70·20	6·12
50	,,	46·61	55·21	3·82
60	,,	55·00	55·30	3·68
80	,,	57·28	37·74	1·68

J. W.

Electrolytic Conductivity of Stereoisomeric Acids. By N. ZELINSKY (*J. Russ. Chem. Soc.*, **23**, 612—632).—The author has examined solutions of various isomeric acids with respect to their electrolytic conductivity, using Ostwald's method. He considered it probable that solutions of stereoisomeric acids, mixed in equal proportions, would give a dissociation constant equal to the mean of the constants of the acids separately, but that structurally isomeric acids would give a value different from the mean. The results of his experiments do not bear out this view, many exceptions occurring.

J. W.

Note by Abstractor.—The author is evidently unacquainted with the theory of isohydric solutions of Arrhenius, according to which equimolecular solutions of any acids would, when mixed, give a dissociation constant nearly equal to the mean of the separate constants, provided that these did not differ greatly from each other. If they did differ to any great extent, then the constant of the mixed solution would fall away considerably from the mean, and would not remain constant for different dilutions. These deductions are amply confirmed by the data obtained by the author. Isomerism does not affect the question directly at all.

Laws of the Expansion of Liquids compared with those relating to Gases and the Form of the Isothermals for Liquids and Gases. By E. H. AMAGAT (*Compt. rend.*, **115**, 919—923).—The coefficient of expansion of liquids by heat diminishes regularly as the pressure increases. It also increases regularly with the temperature; the increase da/dt diminishing as the pressure increases; so that, with ether under a pressure of 1000 atmospheres, the increase is practically nothing, although with alcohol under the same pressure it is still observable. The general form of the isothermals for liquids, taking p as abscissæ and pv as ordinates, is similar to that of the isothermals for gases.

H. C.

Relation between Heats of Formation and Temperatures of Reaction. By M. PRUD'HOMME (*Compt. rend.*, **115**, 1307—1308).—Sulphuric acid combines with potassium hydroxide, sodium hydroxide, and ammonia at the *absolute temperatures* 183°, 193°, and 213° respectively; it acts on metallic potassium at 205° and on sodium at 223°. Nitric acid acts on the alkalis at somewhat lower temperatures than sulphuric acid. Now the heats of formation of the solid salts from the hydrated acid and solid hydrated bases are

$\frac{1}{2}K_2SO_4$	40·7 Cal.	KNO_3....	42·6 Cal.
$\frac{1}{2}Na_2SO_4$.....	34·7 „	$NaNO_3$...	36·1 „
—	—	NH_4NO_3..	34·0 „

It follows that the temperatures of reaction are lower the higher the heats of formation of the product, and this agrees with the law already enunciated by Berthelot.

For the same series of compounds, the product of the heat of formation Q into the *absolute* temperature of reaction T is practically constant. In the case of potassium, sodium, and ammonium sulphates, the numbers are 626, 629, and 601 respectively, and for sodium and potassium nitrates 216 and 213 respectively.

It is well known that in the same series of salts the molecular specific heat M × C is practically constant, and hence

$$Q \times T = K \times M \times C \text{ or } \frac{Q}{M} = K\frac{C}{T}.$$

For the same series of compounds, the heat of formation of the unit of mass is proportional to the specific heat and inversely proportional to the absolute temperature at the point of reaction. C. H. B.

Thermochemistry of Isomeric Allyl and Propenyl Derivatives. By F. Stohmann and H. Langbein (*J. pr. Chem.* [2], **46**, 530—546; compare Abstr., 1890, 100; 1891, 11; 1892, 763).—Eykman (Abstr., 1890, 748) has demonstrated the ease with which the labile allyl derivatives, such as safrole, methyleugenol, &c., may be converted into the stable isomeric propenyl derivatives. The thermochemistry of these was ascertained by combustion in oxygen at 25 atmospheres pressure in a Berthelot's bomb, as already described. The results are given in the following table (p. 154).

It will be noted in each case the change of the labile allyl derivative into the stable propenyl derivative is accompanied by a loss of energy, the heat of combustion of the propenyl derivative being from 8·8 to 11·1 Calories lower than that of the allyl derivative; this is in accord with the other cases which have been studied (compare Abstr., 1890, 100; 1892, 763). Compounds like eugenol and betelphenol, which differ only in orientation, have practically the same heat of combustion. Attention is called to the higher specific gravity refractive index, and melting point of the propenyl derivatives as compared with the allyl derivatives. The ± energy change which accompanies various reactions, such as substitution of OH for H (Abstr., 1892, 763), $CH_2{\cdot}CH{:}CH_2$ for H, and $CH{:}CH{\cdot}CH_3$ for H, are compared with the cases which have been already published. These results, and others shortly to be detailed, confirm the authors in their belief that the opening up of the ethylenic linking by the addition of two hydrogen atoms is not accompanied by a constant accession of energy, as would be deduced from Horstmann's figures (*Ber.*, **21**, 2217).

	Mol. weight.	Heat of combustion at constant pressure per gram molecule, Cal.	Heat of formation, Cal.	Aggregation.
Allyl derivatives—				
Methylchavicol, $C_{10}H_{12}O$	148	1335·1	18·9	liquid.
Eugenol, $C_{10}H_{12}O_2$	164	1286·9	67·1	,,
Eugenol acetate, $C_{12}H_{14}O_3$	206	1498·5	112·5	solid.
Eugenol benzoate, $C_{17}H_{16}O_3$	268	2065·3	84·7	,,
Betelphenol, $C_{10}H_{12}O_2$	164	1286·9	67·1	liquid.
Betelphenol benzoate, $C_{17}H_{16}O_3$	268	2065·4	84·6	solid.
Methyleugenol, $C_{11}H_{14}O_2$	178	1459·4	57·9	liquid.
Safrole, $C_{10}H_{10}O_2$	162	1244·7	40·3	,,
Apiole, $C_{12}H_{14}O_4$	222	1499·6	111·4	solid.
Propyl derivatives—				
Anethoïl, $C_{10}H_{12}O$	148	1324·2	29·8	solid.
Isoeugenol, $C_{10}H_{12}O_2$	164	1278·1	75·9	liquid.
Isoeugenol acetate, $C_{12}H_{14}O_3$	206	1489·0	122·0	solid.
Isoeugenol benzoate, $C_{17}H_{16}O_3$	268	2056·1	93·9	,,
Methylisoeugenol, $C_{11}H_{14}O_2$	178	1448·0	69·0	liquid.
Ethylisoeugenol, $C_{12}H_{16}O_2$	192	1602·9	77·1	solid.
Isosafrole, $C_{10}H_{10}O_2$	162	1234·5	50·5	liquid.
Asarone, $C_{12}H_{16}O_3$	208	1576·8	103·2	solid.
Isoapiole, $C_{12}H_{14}O_4$	222	1489·0	122·0	,,
Anisoïl, C_7H_8O	108	905·5	28·5	liquid.

A. G. B.

Estimation of the Vapour Density of Iodine in different Atmospheres. By E. THIELE (*Zeits. anorg. Chem.*, **1**, 277—284).—The author's experiments were made to ascertain the influence of foreign molecules on the vapour density of iodine. Preliminary experiments in an ordinary V. Meyer's apparatus in atmospheres of nitrogen, oxygen, and hydrogen chloride showed that the presence of these gases is without influence. Further experiments were then made in a modification of this apparatus, which is described with the aid of a drawing. In the presence of ether vapour, and at the temperature of boiling sulphur, iodine gives much lower values for the vapour density than the normal ones; but it was subsequently found that iodine acts on ether at this temperature, so that it is doubtful if the low values are due to dissociation. In the presence of chloroform vapour, a normal value was obtained. A. R. L.

Vapour Pressure of Aqueous Alcoholic Solutions of Salts. By I. KABLUKOFF (*J. Russ. Chem. Soc.*, **23**, 388—391).—The author finds that when sodium chloride is dissolved in a mixture of water and ethyl alcohol, the vapour pressure of the solvent, instead of being lowered, as is the case with a pure liquid, is increased. The following numbers were obtained by him for a mixture of alcohol and water of sp. gr. 0·973 at 20°:—

$t°$.	h.	h'.	$\frac{h-h'}{h}$.	v.
19·5	24·79	25·99	−0·048	1·0
18·5	20·87	24·31	−0·165	0·5

In the table, h denotes the vapour pressure of the solvent, h' that of the solution, and v the number of litres in which 1 gram molecule of the salt is dissolved. J. W.

Density of Sulphuric acid Solutions. By S. U. Pickering (*Phil Mag.* [5], **33**, 463—466). In answer to Rücker's further remarks on this subject (see this vol., ii, 61), the author points out that he did not offer a fresh solution (with one break) of his results, but simply showed that one of the four breaks first mentioned, namely, that which he had always considered to be very feebly marked, could be bridged over by the use of a more complicated parabola, but that there were reasons against the acceptance of this simplification. In the author's opinion, the "no break" curve contributed by Rücker is "an artificial and highly improbable representation of physical facts," whereas his own "four break" representation is not only very probable, but is unique inasmuch as it affords an interpretation in harmony with all the other properties studied. The concordance of these various results, he contends, is, indeed, the chief argument in favour of his views. S. U. P.

Some Experiments on the Diffusion of Substances in Solution. By S. U. Pickering (*Phil. Mag.* [5], **35**, 127—134).—Weak solutions of electrolytes were allowed to diffuse from open jars into very large volumes of water. The rate of diffusion being proportional to the translational velocity of the molecules, the relative values of mv^2 were thus obtained, and these were compared with the osmotic pressures of the solutions as determined from their freezing points. If osmotic pressure is due to the impact of free dissolved or quasi-gaseous molecules, the molecular weights which give the osmotic pressures as constant ought also to give mv^2 as a constant when determined from the rate of diffusion. But this was not found to be the case; the values were 16 times greater in some instances than they were in others. Substances with large molecular weights gave the largest values for mv^2. S. U. P.

Relations of the Physical and Chemical Properties of the Chemical Elements and Compounds. By H. Fritz (*Monatsh.*, **13**, 743—834).—The author has collected data with respect to the cohesion of elements and compounds, and shows that certain relationships hold good between the force of cohesion and other physical and chemical properties. The results have been for the most part already published in other papers. H. C.

Influence of Electrolytic Dissociation on the Decomposition of Ammonium Nitrite in Aqueous Solution. By A. Angeli and G. Boeris (*Gazzetta*, **22**, ii, 349—351).—The fact that concentrated aqueous solutions of ammonium nitrite are much more readily de-

composed by heat than when dilute suggests that this is caused by the electrolytic dissociation in the case of the former being less far advanced than in more dilute solutions. If this be so, the addition to the solution of salts having one ion in common with ammonium nitrite should produce the same effect as an augmentation of concentration. This is found to be the case; the speed of decomposition by heat of dilute ammonium nitrite solutions is greatly increased by the addition of ammonium chloride, ammonium sulphate, potassium nitrite, or sodium nitrite, whilst the addition of sodium chloride, sodium acetate, or magnesium sulphate does not alter the rate of decomposition. The authors are continuing the investigation.

W. J. P.

Cryoscopy, &c., of Ammoniometallic Compounds. By J. PETERSEN (*Zeit. physikal. Chem.*, **10**, 580—592).—The molecular weights of ammoniacal platinum, cobalt, and chromium compounds, as determined from the freezing points of their aqueous solutions, with the help of Raoult's empirical constants, give results agreeing very well with the formulæ usually assumed to be correct. The most marked exceptions are formed by the rhodo- and erythro-salts, which, however, in all probability decompose in solution.

The electrical conductivity of solutions of the same salts was also determined at 18°, and the author presents his results in tabular and curve form. The values of i obtained by the two methods show in general a good agreement.

J. W.

Behaviour of Indole and some of its Derivatives with respect to Raoult's Law. By A. FERRATINI and F. GARELLI (*Gazzetta*, **22**, ii, 245—269).—The high results obtained in molecular weight determinations by the cryoscopic method when naphthalene is used as a solvent, for substances such as indole, β-methylindole, $\alpha\beta$-dimethylindole, carbazole, indene, and α-naphthol have led the authors to investigate the cause.

The molecular depressions of the freezing point of other solvents by these substances are quite normal; the formation of solid solutions on freezing seemed therefore probable (compare Van Bijlert, Abstr., 1891, 1411). By means of a specially constructed apparatus, the crystals deposited on cooling a solution of indole in naphthalene were separated from the solution, then washed with ether, and analysed. Control experiments were also made with solutions of α-methylindole, which gives normal results with naphthalene as a solvent; this was done in order to determine what proportion of the dissolved substance was taken up by the separating crystals as a mere mechanical inclusion. The amount of indole found in the solidified naphthalene was far greater than that of the α-methylindole; the proportion of the latter gives an approximate measure of the quantity of indole carried down mechanically by the naphthalene. The excess of indole found in the naphthalene should, therefore, be present in a state of solid solution, 38—40 per cent. of the indole dissolved crystallises with the naphthalene, and of this only one-half is carried down mechanically. The above explanation is rendered much more

probable by the fact that those substances which give high molecular weights are very similar in constitution to the solvents employed.

Quite another hypothesis must be devised to explain the small depression of the freezing point of naphthalene caused by benzoic acid. The crystals separating on cooling the solution contain only some 3—4 per cent. of the acid present, merely as a mechanical inclusion. Beckmann (Abstr., 1891, 389) found that benzoic acid gives a high molecular weight by the boiling point method in benzene or chloroform solution, but normal values are obtained when acetic acid is used as the solvent; hence it is probable that the benzoic acid is present in such solutions as aggregates of high molecular weight.

W. J. P.

Stereochemistry of Nitrogen. By A. Claus (*J. pr. Chem.* [2], **46**, 546—559).—This is a critique of the paper of Hantszch and Miolati, on "Dissociation Constants of Stereoisomeric Nitrogen Compounds" (Abstr., 1892, 1268). Claus will not admit the necessity for stereoisomeric theories in this connection, position isomerism and kind of linking appearing to furnish sufficient explanation.

A. G. B.

Avidity of Acids in Aqueo-alcoholic Solutions. By I. Kablukoff (*J. Russ. Chem. Soc.*, **23**, 459—487).—From an examination of the electrolytic conductivity of hydrogen sulphate, hydrogen chloride, lithium sulphate, and lithium chloride dissolved singly and together in various mixtures of alcohol and water, the author finds that the "avidity" of hydrogen sulphate with respect to hydrogen chloride is less in solutions containing alcohol than it is in pure water.

J. W.

Affinity of Organic Acids. By P. Walden (*Zeit. physikal. Chem.*, **10**, 563—579, and 638—664; compare Abstr., 1892, 266).—The dissociation constants of the following tribasic acids were measured:—

	K.
Tricarballylic acid, m. p. 158°	0·022
Unsymmetrical methyltricarballylic acid, m. p. 180°.	0·032
Unsymmetrical ethyltricarballylic acid, m. p. 147–148°	0·032
Unsymmetrical propyltricarballylic acid, m. p. 136°.	0·031
Unsymmetrical isopropyltricarballylic acid, m. p. 161°.	0·043
p-Tetramethyltricarballylic acid (?), m. p. 156°	0·0098
a-Tetramethyltricarballylic acid (?), m. p. 133°	0·0111
Citric acid, m. p. 152—154°	0·082
$\beta\gamma$-Dicarboxy-γ-valerolactone, m. p. 168° (decomp.)	0·66
Aconitic acid, m. p. 180—183°	0·136
Ethenyltricarboxylic acid, m. p. 150°	0·32
Propenyltricarboxylic acid, m. p. 146°	3·305
Butenyltricarboxylic acid, m. p. 136—137·5°	0·307
Isobutenyltricarboxylic acid, m. p. 148°	0·334
$\alpha\beta$-Dimethylethenyltricarboxylic acid, m. p. 156—158°	0·503
Benzylethenyltricarboxylic acid, m. p. 168·5°	3·2

	K.
Ethylmethylcarboxyglutaric acid, m. p. 166°	0·974
Propylmethylcarboxyglutaric acid, m. p. 167°.....	1·02
Benzylmethylcarboxyglutaric acid, m. p. 178°..about	1·5
Unsymmetrical trimethylenetricarboxylic acid	0·91
Normal butanetetracarboxylic acid, m. p. 233°	0·040

The constants of a considerable number of aromatic derivatives of fatty acids were determined; those of acetic acid derivatives are given below:—

	K.
Anilidoacetic acid, m. p. 127—128°	0·0038
Acetanilidoacetic acid, m. p. 194—195°.....	0·0260
Chloracetanilidoacetic acid, m. p. 130°.....	0·0340
Bromacetanilidoacetic acid, m. p. 152°.....	0·0340
Acetobromanilidoacetic acid, m. p. 176—177°.....	0·0285
Orthotoluidoacetic acid, m. p. 148—149°	0·00587
Acetorthotoluidoacetic acid, m. p. 210—212°	0·0219
Paratolylglycine (Bischoff, Hausdörfer), m. p. 112—114°	0·0015
Acetylparatolylglycine, m. p. 175—176°	0·0219
α-Naphthylglycine, m. p. 199°	0·004
Aceto-α-naphthylglycine, m. p. 156°.....	0·0207
β-Naphthylglycine, m. p. 133—136°.....	0·006
Aceto-β-naphthylglycine, m. p. 172°.....	0·0241
Phenylimidodiacetic acid, m. p. 150—155°	0·273
Orthotolylimidodiacetic acid, m. p. 158—162°.....	0·209
α-Naphthylimidodiacetic acid, m. p. 133—134°	0·051
β-Naphthylimidodiacetic acid, m. p. 182—183°.....	0·246

Other acids investigated were:—

	K.
Ethylmethylacetic acid, b. p. 175°	0·00170
Diethylacetic acid, b. p. 190°	0·00203
Iodacetic acid, m. p. 82°	0·075
α-Bromopropionic acid, m. p. 15—20°.....	0·108
β-Bromopropionic acid, m. p. 62·5°.....	0·0098
αα-Dibromopropionic acid, m. p. 61°.....	3·3
αβ-Dibromopropionic acid, m. p. 64°.....	0·67
α-Nitrosopropionic acid, m. p. 176—178°.....	0·050
β-Nitropropionic acid, m. p. 65—67°.....	0·0162
α-Bromobutyric acid	0·106

J. W.

Influence of the Constitution of the Alcohols on the Velocity of Etherification. By N. MENSCHUTKIN (*J. Russ. Chem. Soc.*, **23**, 263—283).—The author gives the following table of the velocity constants of etherification for alcohols mixed in molecular proportion with acetic anhydride, diluted with 15 volumes of benzene, and heated at 100°:—

Primary Saturated Alcohols.

	Etherification constant.	Ratio to the constant of methyl alcohol.
$CH_3{\cdot}OH$	0·1118	100·0
$CH_3{\cdot}CH_2{\cdot}OH$	0·0542	48·4
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	0·0480	42·9
$CH_3{\cdot}[CH_2]_2{\cdot}CH_2{\cdot}OH$	0·0465	41·6
$CHMe_2{\cdot}CH_2{\cdot}OH$	0·0401	35·9
$CH_3{\cdot}[CH_2]_5{\cdot}CH_2{\cdot}OH$	0·0393	35·1
$CH_3{\cdot}[CH_2]_6{\cdot}CH_2{\cdot}OH$	0·0377	33·7
$CH_3{\cdot}[CH_2]_{12}{\cdot}CH_2{\cdot}OH$	0·0291	26·0
$CH_3{\cdot}[CH_2]_{14}{\cdot}CH_2{\cdot}OH$	0·0269	24·0
$CH_3{\cdot}[CH_2]_{16}{\cdot}CH_2{\cdot}OH$	0·0245	21·9
$CH_3{\cdot}[CH_2]_{28}{\cdot}CH_2{\cdot}OH$	0·0174	15·5

Primary Unsaturated Alcohols.

$CH_2{:}CH{\cdot}CH_2{\cdot}OH$	0·0287	25·9
$CH_2{:}CMe{\cdot}CH_2{\cdot}OH$	0·0267	23·9
$CH{:}C{\cdot}CH_2{\cdot}OH$	0·0200	17·9
$C_6H_5{\cdot}CH_2{\cdot}OH$	0·0280	25·0

Secondary Saturated Alcohols.

$CHMe_2{\cdot}OH$	0·0148	13·2
$CHMeEt{\cdot}OH$	0·0123	11·0
$C_6H_{13}{\cdot}CHMe{\cdot}OH$	0·00916	8·1

Secondary Unsaturated Alcohols.

$C_3H_5{\cdot}CHMe{\cdot}OH$	0·00643	5·7
$CH(C_6H_5)_2{\cdot}OH$	0·00258	2·3
$CH(CH_2Ph)_2{\cdot}OH$	0·00108	0·96

Tertiary Alcohol.

$CMe_3{\cdot}OH$	0·00091	0·8

Chloro-alcohols.

$CH_2Cl{\cdot}CH_2{\cdot}OH$	0·0113	10·1
$CHCl_2{\cdot}CH_2{\cdot}OH$	0·00262	2·3
$CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}OH$	0·00523	4·5
$CH(CH_2Cl)_2{\cdot}OH$	0·000338	0·3

Cyano-alcohols.

$CN{\cdot}CH_2{\cdot}OH$	0·0461	41·2
$CN{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	0·00896	8·0
$CN{\cdot}CH_2{\cdot}CHMe{\cdot}OH$	0·00305	2·7

Ether Alcohols.

$OAc{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	0·0133	11·9
$COOEt{\cdot}CH_2{\cdot}OH$	0·0263	23·5
$COOEt{\cdot}CHMe{\cdot}OH$	0·00568	5·0

From these numbers, it appears that as the carbon chain in the alcohol lengthens, the constant diminishes, and this also occurs when the alcohol becomes unsaturated. The primary alcohols have a greater constant than the secondary, and these again than the tertiary alcohols. With regard to the substituted alcohols, the author draws a comparison between the influence of the substituting groups on the constant of etherification, and on the dissociation constant of acids as studied by Ostwald. In general, a group which increases the dissociation constant diminishes the etherification constant. J. W.

Rate of Sugar Inversion in Aqueo-alcoholic Solutions. By I. KABLUKOFF and A. TSAKONI [ZACCONI] (*J. Russ. Chem. Soc.*, **23**, 546—559).—The author has obtained the following velocity constants for sugar inversion at 25° in mixtures of alcohol and water under the influence of the acids given in the table :—

Solvent.	HCl.	H_2SO_4.	CCl_3·COOH.	CH_2Cl·COOH.
Water.....	21·30	11·68	15·98	1·08
10 per cent. alcohol ..	20·80	10·82	12·21	0·785
20 „ „ ..	20·11	9·65	11·30	0·632
30 „ „ ..	18·68	8·33 (?)	7·32	0·380
40 „ „ ..	17·61	8·19	6·79	0·250
50 „ „ ..	16·66	7·36	5·12	0·199

Taking the value for hydrochloric acid as 100 in each case, the "affinity" of the acids in the various mixtures appears as follows :—

Acid.	Water.	10 p. c. alcohol.	20 p. c. alcohol.	30 p. c. alcohol.	40 p. c. alcohol.	50 p. c. alcohol.
HCl.....	100·0	100·0	100·0	100·0	100·0	100·0
H_2SO_4.....	54·8	52·2	48·0	45·1 (?)	46·5	44·2
CCl_3·COOH...	75·0	58·7	56·2	39·2	38·6	32·0
$CHCl_2$·COOH .	5·1	3·8	3·1	2·0	1·4	1·2

J. W.

Reaction between Nitrites and Salts of Hydroxylamine. By C. MONTEMARTINI (*Gazzetta*, **22**, ii, 304—325).—The author has studied the velocity of the reaction occurring between hydroxylamine hydrochloride and sodium nitrite in aqueous solution represented by the equation NH_2·OH,HCl + $NaNO_2$ = N_2O + NaCl + $2H_2O$. The velocity is deduced from the general formula $k = \frac{1}{T}\left(\frac{1}{C} - \frac{1}{C_0}\right)$, where k is a measure of the velocity, C_0 the quantity of hydroxylamine initially present in grams per 100 c.c. of the solution, and C the quantity of hydroxylamine present T minutes after the commencement of the reaction. Equivalent quantities of hydroxylamine hydrochloride and sodium nitrite were used.

If C_0 be greater than 0·036 at 16°, k increases considerably as T increases; at this concentration, $k = 0{\cdot}226$ at 25°, and is nearly constant. When T becomes greater than 400, however, the products of the reaction make their presence evident by diminishing k. The addition of sodium chloride, one of the products of the reaction, has a considerable effect on the velocity. When the solution contains 24·3 per cent. of sodium chloride, k falls to 0·026 at 25°; even when this large excess is present, however, k decreases in magnitude for the higher values of T. The velocity becomes much greater as the temperature rises.

The product $k\eta$, where η is the constant of internal friction of the solution, is not a constant for solutions containing varying amounts of sodium chloride, in addition to the reacting constituents. Kajander found that $k\eta$ was constant in a number of reactions between acids and insoluble carbonates; these, however, were all reactions of the first order, one of the active substances being a solid. The present reaction is one of the second order, both the substances being in the liquid state, and the product $k\eta^2$ is approximately constant if large quantities of sodium chloride (16—24 per cent.) or sulphate (8—14 per cent.) be considered.

Sodium sulphate diminishes the speed of reaction in a similar manner to sodium chloride; tabulated results are given of experiments in which varying quantities of sodium sulphate are present in the solution. The author enunciates the law that in a reaction of the nth order, $k\eta^n$ is a constant when the acting substances are present in molecular proportion.

If one of the reacting salts be present in excess, kn should be constant during variations of n, because $-\frac{dC}{dT} = knC^2$, n being the ratio of the number of molecules of the one salt to that of the other. This was not verified, however, when the proportion of sodium nitrite present was varied.

With hydroxylamine hydrochloride, the velocity of reaction is less than when the sulphate is used, and still less than with the nitrate. With lithium, sodium, and potassium nitrites, k decreases as the atomic weight of the metal increases, and k is greater for strontium nitrite than for that of barium. W. J. P.

Isomorphism. Part VII. By J. W. Retgers (*Zeit. physikal. Chem.*, **10**, 529—557; compare Abstr., 1891, 146, and 1151; Abstr., 1892, 1048).—Potassium ferrate, K_2FeO_4, may be preserved for days in solution without undergoing decomposition, and may be crystallised at a gentle heat in microscopic, black prisms or sharp pyramids. It forms mixed crystals with potassium sulphate, selenate, chromate, tungstate, and molybdate, and is, therefore, isomorphous with these salts. The colour of the mixed crystals varies from pink through dark red to dark brown in the case of chromate. No mixed crystals could be obtained with potassium tellurate.

Potassium tellurate when crystallised out of more or less concentrated solutions of caustic potash appears in two forms, namely, feebly birefringent crystals of $K_2TeO_4 + 5H_2O$, and highly birefringent

crystals probably containing 2 mols. H_2O. Most likely it is the latter form which crystallises from potash solution along with potassium osmiate, $K_2OsO_4,2H_2O$, yielding brown, feebly dichroic crystals.

Potassium ruthenate crystallises neither with potassium sulphate and selenate, nor with potassium tellurate and osmiate.

The author gives the following corrected table of the crystallographic relations of the sulphates, selenates, &c., of the potassium group:—

Rhombic { K_2SO_4, Am_2SO_4, Rb_2SO_4, Cs_2SO_4, Tl_2SO_4.
K_2SeO_4, Rb_2SeO_4, Cs_2SeO_4, Tl_2SeO_4.
K_2CrO_4, Rb_2CrO_4, Cs_2CrO_4.
K_2MnO_4, Rb_2MnO_4, Cs_2MnO_4.
K_2WO_4.
K_2MoO_4.
K_2FeO_4.

Monoclinic { Am_2SeO_4.
Am_2CrO_4.
Am_2MoO_4.

Tl_2CrO_4, probably rhombic.

The sulphotungstates and sulphomolybdates of potassium and ammonium do not form mixed crystals with potassium or ammonium sulphate.

The author considers the birefringency and pleochroism of the mixed crystals of ammonium chloride and ferric chloride to be due to the inclusion in the crystal of $Fe_2Cl_6 + 7H_2O$, which is itself birefringent and pleochroic. Roozeboom's assumption that a regular modification of the ferric chloride exists in the mixed crystal, and that the optical properties are occasioned entirely by internal tension, appears to him unnecessary. J. W.

Aluminium Apparatus in the Laboratory. By G. Bornemann (*Ber.*, **25**, 3637—3642).—The author describes the efficiency and appearance of air and water baths, rings, clamps, &c., made of aluminium which he has used in the laboratory for some time. In accordance with the physical and chemical properties of aluminium, he finds that it is preferable to use it in many cases instead of copper and iron. E. C. R.

New Drying Oven. By M. Kaehler (*Ber.*, **25**, 3612—3614).—The speciality of the apparatus consists in an inverted and truncated four-sided pyramid of brass which is inserted in the floor of the oven; it is closed at the top and is surrounded by another pyramid open at the top. The oven is heated by a burner placed under the inner closed pyramid, and the products of combustion pass from the top of this pyramid through four tubes which run up inside the corners of the oven, and help to maintain the temperature of the oven. A current of heated air which enters the oven through the space between the outer and inner pyramids is also continually passing through the oven. E. C. R.

Laboratory Apparatus for Distillation with Superheated Steam. By B. JAFFÉ (*Ber.*, **26**, 123—125).—Although easy on the large scale, the use of superheated steam in the laboratory is troublesome. The author finds that equally good results may generally be obtained by the use of the hot products of combustion of a bunsen flame. A copper tube of about 3—4 mm. diameter passes through the tubulure of the retort, and is bent at right angles outside the retort. The bunsen flame is placed immediately before the slightly expanded opening of this tube, and the heated products of combustion are drawn into it by means of a water pump connected with the receiver or receivers. The inner end of the copper tube may pass into the liquid in the retort, but the author finds it generally better for it to end just at the surface of the liquid. The presence of carbonic anhydride, nitrogen, and excess of atmospheric air does not prove prejudicial. Distillations of glycerol, paraffin, stearic acid, &c., have been successfully carried out by this method. L. T. T.

Inorganic Chemistry.

The Molecular Weight and Refractive Power of Hydrogen Peroxide. By G. CARRARA (*Gazzetta*, **22**, ii, 341—349).—From experiments on the freezing points of aqueous solutions of hydrogen peroxide, Tammann (Abstr., 1890, 106) concluded that the latter substance has the molecular formula H_4O_4. The molecular depressions of the freezing point observed by Tammann differed greatly amongst themselves, and the method by which he deduced the formula H_4O_4 is open to criticism. Using solutions of very different concentrations, the author found the molecular depression of the freezing point to correspond fairly well with the molecular formula H_2O_2. Tammann's discordant results are possibly due to catalytic decomposition of the solutions, induced by the platinum stirrer used by him; the author employed one of glass.

Determinations of the specific refraction of aqueous solutions of hydrogen peroxide also point to the simple formula H_2O_2. The specific dispersion in aqueous solution is less than that of water, $\left(\frac{\mu_{H_\gamma} - \mu_{H_\alpha}}{d}\right) = 0{\cdot}00747$; considering the substance as a compound of water and oxygen, the atomic dispersion of the second oxygen atom is 0·0867.

The absorption spectrum of the blue ethereal solution of the compound of chromic anhydride and hydrogen peroxide shows a band between $\lambda = 6{\cdot}265$ and $\lambda = 5{\cdot}380$. W. J. P.

Critical Examination of the Fundamental Determinations of Stas on Potassium Chlorate. By G. HINRICHS (*Compt. rend.*, **115**, 1074—1078).—The author points out that in Stas's determination of the oxygen contained in potassium chlorate, the value found is a function of the amount of chlorate taken, so that calculated for

30—35 grams of chlorate O = 16, and for 100 grams of chlorate O = 15·98. Precise deductions cannot, therefore, be made from these determinations. H. C.

Phosphorus Iodosulphide. By L. Ouvrard (*Compt. rend.*, **115**, 1301—1303).—Dry hydrogen sulphide has no action on phosphorus iodide at the ordinary temperature, but phosphorus iodosulphide, P_3S_3I, can be obtained (1) by heating phosphorus tri-iodide in a current of hydrogen sulphide at 110—120° until hydrogen iodide is no longer evolved; (2) by dissolving phosphorus, iodine, and sulphur in the proper proportions in carbon bisulphide, evaporating, and heating at 120° in a current of an inert gas; (3) by dissolving iodine in the proper proportions in a solution of phosphorus sulphide in carbon bisulphide. The iodosulphide crystallises from carbon bisulphide in somewhat bulky, brilliant, highly refractive, golden-yellow prisms, which seem to belong to the triclinic system. It is stable in dry air, but slowly decomposes in contact with moist air with evolution of hydrogen sulphide; it dissolves readily in carbon bisulphide, but is only slightly soluble in benzene or chloroform, and still less soluble in ether or absolute alcohol. When heated in presence of air, it melts at about 106° to a viscous liquid which easily remains in superfusion, and at about 300° it burns with formation of phosphoric anhydride, sulphurous anhydride, and iodine; when heated to 300° in a vacuum, it splits up into iodine and phosphorus sulphide. Cold water has very little effect, but hot water decomposes it rapidly, and fuming nitric acid attacks it with explosive violence and production of light.
C. H. B.

Properties of Dry Hydrogen Sulphide. By R. E. Hughes (*Phil. Mag.* [5], **33**, 471—475).—Hydrogen sulphide, dried by passing over calcium chloride and phosphoric anhydride, has no action on magnesia, baryta, ferric oxide, or on salts of silver, copper, mercury, lead, bismuth, arsenic, cadmium, antimony, tin, or cobalt. It does not redden dry blue litmus paper. J. W.

Action of Potassium Permanganate on Sodium Thiosulphate. By C. Luckow (*Zeit. anal. Chem.*, **32**, 53—57).—A solution of sodium thiosulphate, whether neutral, acidified by sulphuric acid, or made alkaline with potash, when boiled with an excess of potassium permanganate, reduces only so much of the latter as corresponds with what is required by the equation $2H_2S_2O_3 + O_7 + H_2O = 2H_2SO_4 + H_2S_2O_6$, and it is stated that the dithionic acid can be detected in the oxidised solution. M. J. S.

Volatilisation of Silica. By E. Cramer (*Zeit. angw. Chem.* 1892, 484—486). — Although a sublimate of pure silica is occasionally observed in the upper region of blast-furnaces, no experiments on the small scale have been recorded to prove its volatility. The author has therefore made some experiments with pure crystallised native silica. A Deville oven, of 12 cm. diameter and 33 cm. in height, was heated by means of graphitic carbon, whilst a blast of air was forced through from below. After two hours, a heat was obtained equal to the highest ever noticed in furnaces; at this

platinum not only rapidly melted, but actually began to boil and to evaporate.

A weighed quantity of crystallised quartz was introduced in a graphitic crucible provided with a lid. This crucible was put inside a magnesite crucible, the empty space being filled up with finely powdered magnesia. The crucibles were now put into the furnace, a strong blast was applied, and, after 4 kilos. of graphite had been burnt, the experiment was stopped and the quartz reweighed, when it was found to have lost 40·5 per cent. in weight. By thrice repeating the fusion, the author succeeded in completely volatilising the quartz. Another experiment showed, that no volatilisation takes place in covered crucibles at the temperature of melting iron.

L. DE K.

Density of Carbonic Oxide, and the Atomic Weight of Carbon. By A. LEDUC (*Compt. rend.*, **115**, 1072—1074).—The carbonic oxide was prepared by the action of sulphuric acid on oxalic acid, and was purified by means of potassium hydroxide, and dried over phosphoric anhydride. Three experiments made in the manner previously described gave, for the weight of the gas at 0° and 760 mm., (i) 2·8470; (ii) 2·8468; (iii) 2·8469 grams: the mean being 2·8469. The weight of air in the same vessel is 2·9440 grams, and hence the relative density of the carbonic oxide is 0·96702. This result agrees with the generally accepted value. Assuming that at 0° this gas has the same molecular volume as oxygen, the atomic weight of carbon, calculated from this determination, is 11·913 (O = 15·88), which agrees very closely with the numbers 11·915 and 11·917, obtained by synthesis by Van der Plaat and Friedel respectively. If the experimental results are taken as correct, the ratio of the molecular volume of carbonic oxide to that of oxygen is 1·0001. It has been shown that the corresponding ratio for hydrogen and oxygen is about 1·002.

If Regnault's value for oxygen (1·10563) is assumed to be true, the atomic weight of carbon would be 11·897, which is not in sufficiently close agreement with the actual determinations, and hence there can be little doubt that the author's value, 1·1050, is more correct.

The relative density of methane, calculated from its molecular weight, is 0·55376, which is lower than the general accepted value; but it is probable that the determinations were made with impure gas.

C. H. B.

Formation of Alkali Carbonates in Nature. By E. W. HILGARD (*Ber.*, **25**, 3624—3630).—The author has determined quantitatively the amount of alkali carbonate which is formed when the solution of an alkali sulphate is treated with precipitated calcium carbonate in the presence of carbonic anhydride. Potassium sulphate, in solutions containing up to 1 gram per litre, is completely converted into potassium hydrogen carbonate. With stronger solutions, the percentage rapidly falls; so that in a solution containing 8 grams per litre, only 26·85 per cent. of the theoretical maximum

of potassium hydrogen carbonate is formed. With sodium sulphate, a similar result is obtained. A complete conversion of sodium sulphate into sodium hydrogen carbonate is obtained in solutions containing up to 0·8 gram per litre. If the solution of the carbonate is evaporated, 9/10ths of the carbonate is reconverted into sulphate.

The author points out the bearing of the results on the formation of alkali carbonates in the soil and on the action of gypsum when applied to the soil. E. C. R.

Solutions of Sodium Silicates. By F. Kohlrausch (*Ann. Phys. Chem.* [2], **47**, 756—764).—The author has studied the electrolytic conductivity of solutions of sodium silicate, Na_2SiO_3, and of solutions containing the base and acid in the proportion Na_2O, $3{\cdot}4SiO_2$, as well as some mixtures of the two with each other and with sodium hydroxide; and from his observations draws conclusions as to the constitution of the solutions examined. If a concentrated solution of the polysilicate is diluted, a long time elapses before the dilute solution attains chemical equilibrium; and, if soda is added to this diluted solution of the polysilicate, equilibrium is again only slowly reached.

The salt Na_2SiO_3 conducts better in dilute solution than equivalent solutions of any other salt. This is owing to hydrolytic decomposition of the salt into acid and base. The same phenomenon is apparent in the case of the polysilicate, only here the dilutions at which the conductivity is very high are much greater than before, as we should expect from the law of mass action. At an equivalent dilution of 100, the numbers obtained for solutions in which the proportion of acid to base varied, pointed to the ratio $2SiO_2 : 1Na_2O$ as being the superior limit of combination of silica with soda. J. W.

Fusion of Calcium Carbonate. By H. Le Chatelier (*Compt. rend.*, **115**, 1009—1011; compare this vol., ii, 117).—The author has repeated the experiments of J. Hall, using a steel tube with an internal coating of nickel. Chemically precipitated calcium carbonate was placed in the tube and heated at 1020° for about an hour. It was thus changed into a completely crystallised rod of calcium carbonate. As in the experiments under high pressures, it was clear that the carbonate had become pasty, but had not completely fused. It follows that the crystallisation of calcium carbonate may be the result of a high temperature only, without the intervention of a high pressure, a result directly opposed to that obtained by Joannis. The difference is doubtless due to the fact that in the author's experiments the tube was suddenly introduced into a furnace previously heated to the required temperature, whilst in the experiments of Joannis the temperature was raised more gradually. Similar differences are observed when sulphur or silica is heated rapidly or slowly, and in these cases the higher melting point observed is due to the formation of a less fusible isomeride during the process of heating. Possibly something of the same kind occurs in the case of calcium carbonate. Chalk crystallises under the same conditions as precipitated calcium carbonate, but calcite undergoes no change even at 1100°.

C. H. B.

Fusion of Calcium Carbonate. By A. JOANNIS (*Compt. rend.*, **115**, 1296—1298).—The author contends that the mass obtained by Le Chatelier (preceding abstract) by heating calcium carbonate at 1020°, not under pressure, had not really been fused, and that its crystalline condition was but little in advance of that of the precipitated carbonate. He has obtained similar results himself, but does not consider that fusion has taken place unless the mass is sufficiently hard to be polished and cut into thin sections. When in this condition, its sp. gr. is 2·57, which is almost identical with that of ordinary marble. Joannis points out that, according to Pictet's translation of Hall's memoir, the latter found that a minimum pressure of 173 atmos. is necessary to obtain complete fusion of calcium carbonate.

C. H. B.

Action of a High Temperature on Metallic Oxides. By H. MOISSAN (*Compt. rend.*, **115**, 1034—1036).—The author has constructed an electric furnace in which an electric arc impinges on a cavity in the middle of two blocks of lime (*Compt. rend.*, **115**, 1031—1033). Different temperatures are obtained by altering the strength of the current. In this paper he describes the effect of the arc on various oxides.

Calcium oxide, with a current of 50 volts and 25 ampères, rapidly becomes covered with brilliant, white crystals of the pure oxide. Similar results are obtained with lime of ordinary purity. With 50 volts and 100 ampères, crystallisation is much more rapid and abundant, and with 70 volts and 350 ampères, the calcium oxide melts completely, and, on cooling, solidifies to a confusedly crystalline mass. *Strontium oxide* crystallises at about 2500°, and at 3000° it melts to a transparent liquid, which, on cooling, solidifies to a confusedly crystalline mass. *Barium oxide* is completely liquid at 2000°, but seems to be stable even at 2500°. On cooling, it forms a mass of confused crystals with a beautifully crystalline fracture. *Magnesium oxide* crystallises less readily than calcium oxide. At about 2500°, it yields transparent crystals, and with 70 volts and 360 ampères, it melts to a transparent liquid. *Aluminium oxide.*—At about 2250°, pure alumina crystallises readily, and if mixed with a small quantity of chromium oxide, it forms ruby-red crystals, inferior, however, to those obtained by Fremy and Verneuil's method. With 25 volts and 75 ampères, the alumina not only melts but completely volatilises. *Chromic oxide*, with 55 volts and 30 ampères, melts to a black mass dotted with black crystals. *Manganese peroxide* melts and evolves oxygen, forming the monoxide, which absorbs some of the lime, and solidifies to a brown, crystalline mass on cooling. *Ferric oxide* melts and loses oxygen, forming the magnetic oxide, partly liquid and partly crystallised. *Nickel oxide* melts, and forms green crystals. *Cobalt oxide* melts somewhat rapidly, and forms rose-coloured crystals. *Titanic anhydride*, with 50 volts and 25 ampères, yields black, prismatic crystals of the monoxide; with 45 volts and 100 ampères, the monoxide melts in three minutes, and is partly dissociated and completely volatilised in eight minutes. *Cupric oxide* is completely decomposed at 2500°, and yields small masses of metallic copper and a crystallised compound of copper and calcium oxides.

Zinc oxide rapidly volatilises, and condenses in long, transparent, crystals at the mouth of the furnace and on the electrodes.

C. H. B.

Decomposition of Aqueous Vapour by Magnesium. By M. Rosenfeld (*Ber.*, **26**, 59—60).—The experimental illustration of the combustion of magnesium in aqueous vapour devised by Moody (Proc., 1891, 20) is substantially the same as that described by the author about ten years ago (*Ber.*, **15**, 161); the same phenomenon can be more simply and elegantly shown by employing powdered magnesium instead of magnesium ribbon, but care has to be exercised in the heating, both of the metal and the water, otherwise the action is very violent.

F. S. K.

Monomagnesium Phosphate. By J. Stoklasa (*Zeit. anorg. Chem.*, **1**, 307—312).—Pure magnesium oxide is dissolved in concentrated phosphoric acid (sp. gr. 1·4), and the solution evaporated on the water-bath until a crystalline pellicle is formed on the surface. The crystals are washed with ether until all the acid is removed, pressed, and dried in a current of air. The compound thus prepared has the composition $MgH_4P_2O_8 + 2H_2O$, and forms nodular aggregates of small crystals; it is non-hygroscopic, and, unlike the calcium salt, is not decomposed by water.

A. R. L.

Determination of the Atomic Weight of Cadmium. By W. S. Lorimer and E. F. Smith (*Zeit. anorg. Chem.*, **1**, 364—367).—Carefully purified cadmium oxide was dissolved in potassium cyanide, and the cadmium deposited electrolytically. From the ratio of the weight of the oxide to that of the metal, the atomic weight of cadmium was determined, the arithmetical mean of nine determinations giving the number 112·055 (O = 16). The highest result was 112·182, and the lowest 111·908.

H. C.

Possibility of the Existence of certain Metals in the Gaseous Condition at Temperatures below their Fusing Points. By W. Spring (*Zeit. anorg. Chem.*, **1**, 240—244).—By passing a current of hydrogen through a heated glass tube containing the volatile chlorides of copper or iron, a lustrous, metallic deposit is formed on the sides of the tube, which proves on examination to have a crystalline structure, whereas the metal obtained by similarly reducing the oxides is pulverulent and devoid of crystalline form. The chlorides of cobalt, nickel, chromium, uranium, and tungsten were also examined, and it was found that the reduced metal is crystalline in those cases only where the salts are volatile. Silver chloride is reduced at a temperature below that at which it volatilises, and here a spongy, crystalline mass of metal having no lustre is obtained. The author is of opinion therefore, that after the chlorine has been removed by the hydrogen from the volatile chlorides, the metals exist for a time in the gaseous condition. As, however, the metals mentioned are only volatile at temperatures far above those at which their chlorides suffer reduction, it is assumed that they exist in allotropic modifications, perhaps in the atomic condition. Schützenberger's view (Abstr., 1891, 1429)

as to the existence of a volatile nickel hydrochloride may also be applied to other metals, but fails to throw any further light on the phenomena above described. When silver, platinum, or gold, in the form of leaf, is heated at 150° in a sealed tube with hydrochloric acid, the metal dissolves, but the chloride is subsequently reduced by the hydrogen formed during the interaction, and the metal reappears as microscopic crystals on the sides of the tube. It is possible in this case that even the platinum exists for some time in the liquid condition previously to assuming the crystalline form. A. R. L.

New Formation of Basic Sulphates of Copper. By L. Marchlewski and J. Sachs (*Zeit. anorg. Chem.*, **1**, 405—406).—If a saturated aqueous solution of copper sulphate is heated on a water bath with excess of dimethylaniline or diethylaniline, a bluish-green precipitate is formed which on examination is found to have the composition $6CuO,2SO_3,5H_2O$. It appears to be identical with the basic sulphate of copper already obtained in other ways by Reindel, Pickering, and Habermann. If copper sulphate solution is heated with quinoline, a salt of the composition $8CuO,3SO_3,10H_2O$ is obtained. This salt has not been before observed; it has a bright-green colour, and decomposes when heated to 200°. H. C.

Formation of Aluminium Sulphide. By A. H. Bucherer (*Zeit. angw. Chem.*, 1892, 483—484).—The author has succeeded in economically preparing on the large scale aluminium sulphide, hitherto obtained by passing the vapour of carbon bisulphide over red hot alumina. A mixture of alumina and charcoal is strongly heated in an earthenware retort, and by means of an earthenware tube sulphur is from time to time introduced into the retort. The alumina is gradually completely converted into the corresponding sulphide.

The author thinks that aluminium sulphide may become of great importance in the metallurgy of aluminium. L. de K.

Amorphous, Hydrated Ferric Oxide; Crystalline Ferric Hydroxide; Potassium and Sodium Ferrites. By J. M. van Bemmelen and E. A. Klobbie (*J. pr. Chem.* [2], **46**, 497—529).—Rousseau claims to have obtained crystallised ferric hydroxide, Fe_2C_3,H_2O, by heating hydrated ferric oxide in molten alkali salts (Abstr., 1888, 917, 1034, 1252), and by decomposing ferric oxychloride by water (Abstr., 1890, 1063). Brunck and Graebe obtained the same compound (Abstr., 1881, 126). The results of the authors' reinvestigation of this matter are as follows:—(1.) The hydrous ferric oxide obtained by decomposing potassium nitroprusside, or Roussin's salt (compare Pavel, Abstr., 1883, 297) with alkali hydroxides, and gelatinous hydrated ferric oxide which has been exposed to a low temperature, are amorphous, and of inconstant composition. (2.) Continued heating with a strong solution of potassium or sodium hydroxide converts ferric oxide into a ferrite which is partially soluble and gradually becomes crystalline. In potassium hydroxide solution, the crystals are at first rhombic (?) plates, but as

the heating is continued and the water expelled they become regular octahedra, which are also formed when ferric oxide is heated in fused potassium carbonate or chloride. In sodium hydroxide, the crystals are, at first, crossed prisms, but afterwards hexagonal plates, sometimes becoming rhombohedric and spherical, or long needles; the same are formed when ferric oxide is heated in fused sodium carbonate or chloride. All these crystals have the composition Fe_2O_3,K_2O and Fe_2O_3,Na_2O, respectively. (3.) These crystals (with the exception of the hexagonal plates) are decomposed by water, assuming at first a pseudocrystalline form and then becoming amorphous, hydrated ferric oxide. (4.) The hexagonal sodium ferrite yields Fe_2O_3,H_2O when treated with water; this has the same crystalline form, transparency, and optical properties as the original ferrite; it is not hygroscopic, but begins to lose water below 100°, whereas göthite can be heated to 300° without losing water. (5.) Rousseau's crystalline ferric hydroxide (*loc. cit.*) is, in the authors' opinion, a pseudocrystalline hydrated ferric oxide formed by the decomposition of a ferrite by water (compare 3).

A. G. B.

Action of Metallic Molybdenum and Tungsten on Solutions of Silver, Gold, and other Metals. By E. F. Smith (*Zeit. anorg. Chem.*, **1**, 360—363).—Metallic molybdenum precipitates silver from a solution of silver nitrate, the solution becoming turbid through separation of molybdic acid. If a solution of silver oxide or chloride in ammonia is taken, the turbidity is avoided. The reaction is quantitatively complete, one atom of molybdenum precipitating six of silver. In the case of the chloride, the solution evidently must contain the hexachloride, $MoCl_6$, and this is also formed when molybdenum precipitates gold from auric chloride, a quantitative reaction in which one atom of molybdenum precipitates two of gold. The colour of the resulting solution in the two last instances is a dark-brown. Tungsten acts towards silver and gold solutions very like molybdenum, the action in the case of gold being, however, somewhat slower. Neither metal has any action on neutral, alkaline, or acid solutions of lead nitrate. Molybdenum reduces neutral mercuric chloride at once to mercurous chloride, and eventually to metallic mercury. Tungsten only acts slowly and forms mercurous chloride. Both metals precipitate copper from solutions of copper salts, but the action is not a complete one. Solutions of bismuth and cadmium are unaffected by either metal, and platinum, palladium, and rhodium chlorides only undergo partial reduction. H. C.

A Crystalline Alloy of Iron and Tungsten. By T. Poleck and B. Grützner (*Ber.*, **26**, 35—38).—A lump of iron-tungsten alloy, obtained by an electrolytical method from Bohemian wolframite, was found to consist of a crystalline ground-mass, of the composition $Fe_2W_3C_3$, in the crevices of which were small crystals of the composition FeW_2. The latter form trigonal prisms which belong to the hexagonal system, and are either trapezohedral-tetartohedral, or else rhombohedral-hemihedral and hemimorphous along the primary

axis. Both the crystals and the crystalline matrix are silver-grey, very heavy, and very hard—about as hard as corundum.

C. F. B.

Action of Potassium and Sodium Hydroxides on Antimony Trioxide. By H. Corrimboeuf (*Compt. rend.*, **115**, 1305—1307).—When a solution of 2 parts of potassium hydroxide in an equal quantity of water holding in suspension 1 part of precipitated antimony trioxide, is boiled for a few minutes, rhombic prisms that act strongly on polarised light are formed. They have the composition $K_2O,3Sb_2O_3$, are easily decomposed by cold water, and, when exposed to air, rapidly absorb carbonic anhydride with formation of potassium carbonate and separation of antimony oxide.

If to a boiling solution of potassium hydroxide in its own weight of water, antimony oxide is added in successive small portions until it ceases to dissolve, and the liquid is allowed to cool, the compound $K_2O,3Sb_2O_3,3H_2O$ crystallises in rectangular lamellæ which act on polarised light and show longitudinal extinction.

When water is added gradually to the anhydrous or hydrated triantimonite, the salt is decomposed with separation of prismatic antimony oxide, but as soon as the water, by decomposition of the salt, has become charged with 5 per cent. of potassium hydroxide, octahedral antimony oxide is formed, and when the proportion of hydroxide in solution reaches 20·9 per cent., decomposition ceases. The octahedral oxide obstinately retains 0·6—0·2 per cent of alkali.

If a boiling solution of 1 part of sodium hydroxide in 2 parts of water is saturated with antimony trioxide, and the liquid is then poured into a large quantity of boiling water, and the mixture is filtered, the liquid as it cools, deposits quadratic tables which adhere strongly to the glass. They have the composition $Na_2O,Sb_2O_3 + 6H_2O$, and recrystallise from pure water in octahedra with a square base, but with the same composition. This salt has already been described by Terreil, who obtained it in a somewhat different manner.

If a boiling solution of 1 part of sodium hydroxide in 2 parts of water is mixed with successive quantities of antimony oxide until it ceases to dissolve, and the liquid is allowed to cool, monoclinic needles of the composition $2Na_2O,3Sb_2O_3 + H_2O$ separate.

When a similar solution of sodium hydroxide is boiled with an excess of antimony oxide, the liquid, whilst still warm, deposits rhombic tables of the composition $Na_2O,2Sb_2O_3$. If the liquid, instead of being boiled, is heated with the excess of antimony oxide at 100°, it deposits at that temperature rectangular tables of the composition $Na_2O,3Sb_2O_3$.

All the sodium antimonites alter rapidly in moist air, with formation of sodium carbonate and separation of amorphous antimony oxide. Pure water, either cold or hot, decomposes them with separation of prismatic antimony oxide, which obstinately retains 0·55—0·64 per cent. of alkali. The sesquiantimonite, diantimonite, and triantimonite undergo no alteration in contact with solutions of sodium hydroxide containing respectively 94·3, 188·6, and 113·2 grams per litre.

It is noteworthy that sodium hydroxide yields three antimonites, all of which yield antimony oxide in the crystalline form of valentinite when they are decomposed by water, whereas potassium hydroxide yields only one antimonite, but this, when treated with water, yields antimony oxide crystallised in the forms of both valentinite and senarmontite. C. H. B.

Action of Bismuth on Hydrochloric acid. By A. Ditte and R. Metzner (*Compt. rend.*, **115**, 1303—1305).—Bismuth is not attacked by gaseous hydrogen chloride at the ordinary temperature, nor at any temperature up to the softening point of glass. In contact with a dilute or concentrated solution of the acid, bismuth liberates no hydrogen either under ordinary pressure or in a vacuum, nor even after the bismuth has been in contact with a solution of some metallic chloride which can deposit a thin layer of some other metal on its surface. Sometimes bismuth is found in the solution, although no gas has been liberated, but this only happens when oxygen has not been entirely excluded.

When left in contact with aërated water free from carbonic anhydride, bismuth, after a long time, becomes covered with small crystals of the hydrated oxide, but no bismuth goes into solution.

It follows that bismuth, like antimony, is not attacked by hydrochloric acid except in presence of oxygen, and the readiness with which arsenic, antimony, and bismuth separately dissolve in the acid in presence of oxygen is in intimate relation with their respective heats of oxidation. C. H. B.

Ammoniacal Derivatives of Ruthenium Chloride. By A. Joly (*Compt. rend.*, **115**, 1299—1301). — Anhydrous ruthenium chloride rapidly absorbs dry ammonia at the ordinary temperature with considerable development of heat, and absorption is only complete when the substance is cooled to 0°. The product has then the composition $Ru_2Cl_6 + 7NH_3$, and if gradually mixed with water, it partially dissolves, forming an intense violet-red liquid, but solution is only complete if the water is saturated with ammonia. Similarly, if finely divided anhydrous ruthenium chloride is projected in successive small quantities into a solution of ammonia saturated at a low temperature, and the mixture is heated for some time at 40°, a very deep red solution is obtained which, when sufficiently concentrated, deposits small, crystalline lamellæ of the composition $Ru_2Cl_4(OH)_2,7NH_3,3H_2O$. The crystals are brown with a metallic lustre by reflected light, and yellow by transmitted light; the solution is red by transmitted light, and has a violet tinge by reflected light. 1 part of the compound in 10,000 parts of water has an intense red colour, and even 1 part in 5,000,000 parts of water has a distinct rose colour. The dry salt is stable when exposed to light, but its solutions decompose with precipitation of the brown sesquioxide. Decomposition is rapid when the solution is boiled, and intermediate products are formed either by loss of ammonia or by progressive substitution of the elements of water for chlorine.

When concentrated hydrochloric acid is added to concentrated solutions of the ammoniacal hydroxychloride, the compound

$$Ru_2Cl_4(OH)_2,7NH_3,HCl + 3H_2O$$

separates as a brown precipitate. When dissolved in water, it forms a yellow solution, but as the proportion of water is increased, the colour changes to red. A small quantity of ammonia or other alkali changes the colour at once to reddish-violet. By double decomposition with silver nitrate in acid solution, the hydrochloride of the hydroxychloride yields readily crystallisable salts, forming yellow solutions which become red on the addition of a base.

The red coloration that appears on boiling an ammoniacal solution of the nitroso-oxychloride is due to the formation of the ammoniacal hydroxychloride now described, and is not due to the reproduction of the original nitrosochloride by loss of ammonia. C. H. B.

Mineralogical Chemistry.

Artificial Production of Rutile. By L. Michel (*Compt. rend.*, **115**, 1020—1021).—When an intimate mixture of titaniferous iron ore 1 part, and pyrites 2·5 parts, is heated in a graphite crucible at about 1200° for several hours and allowed to cool, a crystalline mass is obtained which has all the chemical and physical properties of pyrrhotine.

The mass is full of cavities, to the walls of which are attached elongated, quadratic prisms of rutile, identical in every respect with the natural crystals. They are uniaxial and positive, have a deep blue colour and adamantine lustre, are infusible before the blowpipe, and are not attacked by acids; hardness = 6; sp. gr. = 4·28.

The pyrrhotine has the composition Fe_8S_9, and is in crystalline masses with a lamellar texture and a bronze-yellow colour; hardness 4; sp. gr. 4·5. It is slightly magnetic. C. H. B.

Minerals from Lower Silesia. By B. Kosmann (*Jahrb. f. Min.*, 1893, i, Ref. 9—10; from *Zeit. deutsch. geol. Ges.*, **42**, 794—796).—Chrome-iron ore occurs in a serpentine in a vein 7 metres in thickness at Tampadel. The ore contains inclusions of magnetite and spinel. Analysis gave results varying within the following limits:—

Cr_2O_3.	MgO.	SiO_2.	FeO.	Al_2O_3.
35—42	14—16	4—6	18—22	18—22

A specimen of ore from the Bergmannstrost mine consists of iron pyrites, arsenical pyrites, blende, and tetrahedrite with dolomite. In a cavity in the mass there are twin crystals of bournonite covered with dolomite and barytes. B. H. B.

Palygorskite. By P. Zemiatschensky (*Jahrb. f. Min.*, 1893, i, Ref. 33—34; from *Bibl. géol. Russ.*, **6**, 90).—The name of palygorskite was given in 1860 by Savtschenkoff to a fibrous mineral resembling asbestos from the government of Perm. Since that date the mineral has been found at various localities in Russia in Permian and Tertiary beds, and has repeatedly been analysed. A specimen from Nijni-Novgorod was analysed by the author with the following results:—

H_2O.	CaO.	MgO.	Al_2O_3.	SiO_2.	CO_2.
19·68	10·52	8·30	13·93	44·40	3·17

B. H. B.

Composition of Melilite. By G. Bodländer (*Jahrb. f. Min.*, 1893, i, Mem. 15—21).—The author has analysed some good specimens of melilite from Monte Somma with the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
41·34	10·37	4·29	33·84	5·79	1·13	3·45	0·08	100·29

Comparing his results with the published analyses of artificial and natural crystals of melilite, the author concludes that the optically negative melilites are metasilicates of the formula SiO_3R'', isomorphously mixed with the aluminate R'''_2O_4R'', whilst in the optically positive melilites, the aluminate $R'''_2O_6R''_3$ is in isomorphous mixture with the silicate SiO_3R''. In conclusion, the author brings forward arguments disproving Vogt's theory (Abstr., 1892, 1410) that melilite is a mixture of gehlenite and akermanite. B. H. B.

Pholidolite from Sweden. By G. Nordenskjöld (*Jahrb. f. Min.*, 1893, i, Ref. 20—21; from *Geol. Fören. Förhandl.*, **12**, 348).—At Taberg, in Wermland, pholidolite occurs in greyish-yellow, micaceous laminæ, having a sp. gr. of 2·408. Analysis gave the following results:—

SiO_2.	Al_2O_3.	MgO.	FeO.	MnO.	K_2O.	H_2O.	Total.
49·78	6·31	27·94	4·08	0·12	5·93	5·49	99·65

Other minerals occurring in the same cavities are:—garnet, diopside, epidote, apatite, titanite, magnetite, calcite, galena, and chlorite. B. H. B.

Existence of the Diamond in the Meteoric Iron of the Cañon Diablo. By C. Friedel (*Compt. rend.*, **115**, 1037—1041).—A specimen of meteoric iron from the Cañon Diablo was found by Le Bel to contain diamonds, and the specimen found by Eckley Coxe (Abstr., 1892, 947) was cut in two, and a portion weighing 34 grams was treated successively with hydrochloric acid, aqua regia, and hydrofluoric acid. The residue contained minute rounded grains, which had all the properties of carbonado, and which when heated to redness in oxygen formed carbonic anhydride. There can, therefore, be no doubt of the existence of diamonds in the meteorite. The diamonds were not uniformly distributed in the specimen examined, but were

concentrated in and about nodules of iron sulphide and phosphide. The sp. gr. of the grains was slightly higher than 3·3; the sp. gr. of carbonado varies between 3·0 and 3·41. C. H. B.

Hepatic Mineral Water and Mud of the Valle del Gallo. By A. AGRESTINI (*Gazzetta*, **22**, ii, 287—298).—The hepatic spring of the Valle del Gallo is distant about 12 kilometres from Urbino, and 24 from Pesara. Its waters are reputed to have considerable medicinal value. The water has a strong odour of hydrogen sulphide, and issues at a temperature of 14·0—14·2°; its sp. gr. = 1·00274 at 24°; 1000 grams at 14° and 760 mm. contain the following constituents:—

CO_2 (free).	H_2S (free).	Oxygen.	Nitrogen.
70·212 c.c.	43·06 c.c.	0·625 c.c.	17·41 c.c.

$CaH_2(CO_3)_2$.	$MgH_2(CO_3)_2$.	$NaHCO_3$.	NH_4HCO_3.
0·5228 gram	0·0089 gram	0·0262 gram	0·0043 gram

$FeH_2(CO_3)_2$.	$CaSO_4$.	$MgSO_4$.	Na_2SO_4.	Na_2SiO_3.
0·0017 gram	1·5558 grams	0·4501 gram	0·0330 gram	0·0012 gram

$AlPO_4$.	KCl.	NaCl.	NaHS.	SiO_2 (free).
0·0005 gram	0·0281 gram	0·1542 gram	0·0048 gram	0·0437 gram

0·1071 gram of organic matter and traces of manganese and arsenic are also present. The solid residue from 1000 grams dried at 180° weighs 2·7923 grams.

The mud taken from the hole in which the water collects is applied externally to cases of skin disease, etc., with good results. After drying at 125°, it has the following percentage composition:—

$(NH_4)_2SO_4$.	$CaSO_4$.	$Ca_3(PO_4)_2$.	$CaCO_3$.	$MgCO_3$.	NaCl.
0·199	1·470	0·181	25·342	6·044	0·011

K_2O.	Na_2O.	MgO.	Al_2O_3.	Fe_2O_3.	SiO_2 (comb.).	SiO_2 (free).
3·356	2·345	2·964	11·676	6·573	23·390	9·184

S (free).	$BaSO_4$. Mn, As.	Organic matter and H_2O.
0·458	traces	6·253

W. J. P.

Physiological Chemistry.

Influence of Acids and Alkalis on the Determination of the Osmotic Pressure in relation to the Red Blood Corpuscles. By H. J. HAMBURGER (*Rec. Trav. Chim.*, **11**, 61—75).—Acids and alkalis modify the permeability of the blood corpuscles for their different constituents. Acids and alkalis act in opposite ways; the action of an acid can be neutralised by an alkali, and *vice versâ*.

The permeability of the red corpuscles for hæmoglobin is modified in the following way:—After being acted on by acids, they lose their colouring matter in a solution of sodium chloride, but it must be stronger than was necessary before such action took place; they keep their pigment after the action of an alkali in a more dilute solution of sodium chloride than before this action.

Thus, the red corpuscles begin to lose their hæmoglobin in a 0·56 per cent. solution of sodium chloride; but, after the action of a dilute acid, the strength of the solution must be increased to 0·67 per cent., and, after the action of dilute alkali, it must be diminished to 0·51 per cent.

When the attractive force for water (osmotic pressure) is determined, it is necessary to take account of such facts, otherwise the results will be valueless.

Errors can be avoided by carefully neutralising, and by determining the attractive force for water in the neutral fluid. There is, however, still to be subtracted from the number found the attractive force for water of the acid or alkali employed in neutralisation, and, further, to take into account the dilution which results from this operation.

W. D. H.

Occurrence of Glycogen in Blood. By HUPPERT (*Chem. Centr.*, 1892, ii, 873; from *Centr. Physiol.*, **6**, 394).—The author confirms the presence of glycogen in blood. It seems always to be present, but in quantities varying with the kind of blood, and the amount is always very small: ox blood contains 5—10 milligrams per litre.

Glycogen occurs invariably in pus and in larger amounts than in blood; the pus corpuscles contain it in larger amount than does the serum.

A. J. G.

Acid Reaction of Muscle. By F. A. MEYERHOLD (*Chem. Centr.*, 1892, ii, 835—836; from *Sitzber. Physik.-med. Soc. Erlangen*, **24**, 128—155).—It seems probable that living quiescent muscle contains a small quantity of lactic acid, or, at least, of some substance having an acid reaction. In an indifferent liquid, such as distilled water or physiological salt solution, where the disturbing influence of putrefaction is prevented by the action of cold (not by antiseptics), the muscle yields, after a time, a certain amount of acid. This amount is increased by raising the temperature to 45°, but is diminished by cooling. Heating to the boiling point suspends the process for a short time, but does not terminate it, neither is it destroyed by alcohol. The author then points out that the amount of lactic acid found is incompatible with the theory that it is derived from the glycogen in the muscle.

A. J. G.

Accumulation of Potassium Bromide in the Organism. By C. FÉRÉ and L. HERBERT (*Compt. rend. Soc. Biol.*, 1891, 769—771, 807—809).—In man, potassium bromide accumulates in the organs, especially in the brain, liver, and kidneys.

Two cases of epileptics are recorded; they had been treated with this drug for long periods. The amounts found per cent. *post mortem* are given in the following table.

	Case 1.	Case 2.
Brain	0·073	0·090
Lung	0·082	0·156
Liver	0·104	0·137
Spleen	0·133	0·210
Kidney	0·100	0·216
Pancreas	0·043	—
Muscles	0·062	0·160
Cartilages	0·041	0·170
Bones	0·087	0·240
Blood	—	0·270
Testes	—	0·280

These cases show that there is an accumulation of the salt in the tissues; and in the case (No. 2) where the treatment was continued longest (five years), the tissues, where the accumulation is greatest, are those where the nutrition is slow, like the bones and cartilages.

Similar observations were made on animals, rabbits and guinea-pigs, the salt being given subcutaneously. After a few days the animals died, and their bodies were incinerated. Considerable quantities of the salt were found in the ash, showing that its elimination during the first few days is slow. The individual organs were not investigated. W. D. H.

Nutritive Value of Asparagine. By S. Gabriel (*Zeit. Biol.*, **29**, 115—124). **Remarks on the above.** By K. Voit (*ibid.*, 125—128). —The first of these papers is a criticism of that recently published by Politis (this vol. ii, 27). Voit's remarks point out that Gabriel does not contradict Politis in the statement that asparagine is not a proteïd-sparing food, but that he merely states that asparagine has a beneficial effect by promoting the absorption of starchy food.

W. D. H.

Metabolism in Diabetes Mellitus. By F. Voit (*Zeit. Biol.*, **29**, 129—146).—Dieting experiments on diabetic patients, compared with similar ones on healthy people, do not show any very great difference in the general course of metabolic activity. More proteïd is, however, used by diabetics, carbohydrate not being available as a proteïd-sparing food. Experiments on gas exchange also show that more fat undergoes combustion in diabetics as compared with the normal.

W. D. H.

Behaviour of Galactose in Diabetics. By F. Voit (*Zeit. Biol.*, **29**, 147—150).—Although galactose will not increase the hepatic glycogen (C. Voit and others, Abstr., 1892, 902), it causes an increase of the sugar in diabetes. The experiment was made on the same patient as was formerly experimented on in connection with lactose (F. Voit, *ibid.*, 903). The result obtained was the same as with lactose, and is capable of a similar explanation. W. D. H.

Occurrence of Ammonia in the Stomach Contents. By T. Rosenheim (*Chem. Centr.*, 1892, ii, 749; from *Centr. Klin. Med.*, **13**, 817—819).—The stomach contents are filtered, the proteïds removed

by acetic acid and tannin, and the estimation of the ammonia then proceeded with according to Schloesing's method. In healthy subjects, ammonia was found in all phases of digestion and after the ingestion of the most varied foods; the amount being, as a rule, from 0·1 to 0·15 per mille. In many diseases of the stomach, the values still lie within these limits, but occasionally are found to be higher.

It is not possible to estimate the amount of ammonium chloride in the stomach contents, but it must be taken into consideration when estimating the total chlorine: hitherto it must have been calculated as hydrochloric acid. A. J. G.

Uroerythrin and Hæmatoporphyrin in Urine. By L. Zoja (*Chem. Centr.*, 1892, ii, 748—749; from *Centr. med. Wiss.*, 1892, 705—706).—Uroerythrin is characterised by (1) its absorption spectrum—two bands of about equal intensity at about λ 550—525—λ 510—484, the interspace also showing absorption; (2) the great sensitiveness of its solution to light; (3) the green coloration which it gives with alkalis; (4) the properties of the precipitates with urates and with salts of lead, potassium, and barium. Uroerythrin probably occurs in the urine as a salt (sodium salt) in combination with urates.

Hæmatoporphyrin is characterised by (1) the spectra of its acid and alkaline solution; (2) the properties of its metallic compounds; (3) the evolution of pyrroline when heated in the dry state; (4) the scatole-like odour and formation of a uribilinoïd substance when treated with zinc and hydrochloric acid; (5) a reaction resembling Gmelin's with nitric acid. Hæmatoporphyrin from urine is identical with that obtained by the action of reducing agents on hæmatin. McMunn's hæmatoporphyrin is, at least as a rule, a mixture of urobilin and hæmatoporphyrin. Hæmatoporphyrin probably occurs as such in the urine; it is found in the most varying proportions.

A. J. G.

Behaviour of Xylenes in the Organism. By A. Curci (*Chem. Centr.*, 1892, ii, 538; from *Ann. Chim. Farm.*, **16**, 3).—The xylenes show a double action, an irritant action such as is characteristic of phenols and the paralysing action characteristic of aromatic hydrocarbons. The paralysing action is shown most strongly by orthoxylene, less strongly by metaxylene, whilst paraxylene occupies a mean position between the other two. The irritant action is strongest with the para-compound, less with the ortho-, and still less with the meta-compound. The explanation of the irritant action is, that the xylenes suffer partial conversion in the organism into the xylenols, but to an unequal extent, the para-compound being the most affected. A. J. G.

Influence of the Carboxyl Group on the Toxic Action of Aromatic Compounds. By M. Nencki and H. Boutmy (*Chem. Centr.*, 1892, ii, 655—656; from *Arch. expt. Path. Pharm.*, **30**, 300—310).—Many poisonous aromatic compounds become relatively non-poisonous when the carboxyl group is introduced into the molecule, seemingly through the greater stability thus induced. Thus

benzoic acid is less poisonous than benzene, and the same seems to be true as regards naphthalenecarboxylic acid and naphthalene. The same relations hold for the hydroxylated derivatives of benzene and their carboxylic acids; thus whilst orthamidophenol is less poisonous than aniline, ortho- and para-amidosalicylic acids are harmless. Orthoxycarbanilcarboxylic acid is less poisonous than oxycarbanil; it passes through the organism without causing discomfort and can be detected in the urine. Malonanilic acid is a less powerful poison than acetanilide, of which it may be regarded as a carboxylated derivative; it can pass into the urine, and the ingestion of its sodium salt is not followed by an increase in the ethereal hydrogen sulphates in the urine. A like relation is observed between paraphenacetinic acid and phenacetine.

The sulphonic group in replacing hydrogen seems to exert an influence on physiological action resembling that described above for the substitution of the carboxyl group for hydrogen. A. J. G.

Physiological Effect of Opium Smoke. By N. Gréhant and E. Martin (*Compt. rend.*, **115**, 1012—1014).—Opium smoke produced at a temperature of 250°, as is done by actual smokers (this vol., i, 226), has scarcely any effect on a dog. It is without influence on the energy of the contractions of the heart, and the only difference observable is that when anesthæsia is produced by means of a mixture of chloroform and alcohol, the period of agitation at the beginning is shorter with an animal that has been submitted to the action of opium smoke than with one that has not. It is clear that there is a distinct difference between the central nervous systems of the dog and man.

One of the authors smoked successively 20 pipes containing altogether about 4 grams of *chandoo* or prepared opium. After the fourth pipe, frontal headache began, and after the sixth, the headache became general; at the tenth, vertigo set in and continued until the end of the experiment. Half an hour after the smoking stopped, the headache and vertigo began to decrease, and at the end of an hour had quite disappeared. The curve of respiration at the end of the experiment had a somewhat smaller amplitude than at the beginning, and the pulsations of the heart were rather less frequent.

C. H. B.

Toxicity of certain Mineral Salts. By C. Richet (*Compt. rend. Soc. Biol.*, 1891, 774—775).—The salts used were bromides, chlorides, and iodides of lithium, potassium, and rubidium. The results show that the toxic dose is proportional to the molecular weight of the salt and not to its absolute weight. A molecule of rubidium iodide, which weighs 207, is as poisonous as a molecule of lithium chloride, which only weighs 42.

Microbes show great resistance to the toxic action of potassium salts. Mercury is the metallic poison which is most active; it is weight for weight ten times more toxic than copper. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

An Organised Ferment from Cherry Tree Gum. Pectinose. By F. Garros (*J. Pharm.* [5], **26**, 535—537).—Cherry tree gum left in a sterilised flask liquefies after some time, and a yeast-like microbe is found therein, which is more active in presence of ammonium tartrate and is rendered inactive on the addition of hydrochloric acid (5 per cent.). This ferment liquefies plum and cherry tree gums but not gum arabic. The author states that, whereas the precipitate yielded by ferric sulphate with arabin is insoluble in potassium hydroxide solution, that afforded by pectin dissolves at once, and these substances are further distinguished since strong solutions of arabin are rendered insoluble by pure concentrated sulphuric acid, whilst pectin is converted into a sugar which he calls pectinose; this sugar may also be made from beet husks by boiling them with dilute hydrochloric acid for some time, and isolated by precipitating with basic lead acetate and then treating the lead compound with hydrogen sulphide. T. G. N.

Exchange of Carbonic Anhydride and Oxygen between Plants and the Atmosphere. By T. Schloesing, Jun. (*Compt. rend.*, **115**, 1017—1020).—Woolly feather-grass was sown on quartzose sand early in July, and the ratio of carbonic anhydride decomposed to oxygen set free was determined from time to time between the date of sowing and September 6th, when the crop, which was well developed, was cut.

$\frac{CO_2 \text{ disappeared}}{O \text{ liberated}}$ =	Aug. 13.	Aug. 18.	Aug. 26.	Sept. 1.	Sept. 6.
	0·87	0·88	0·88	0·91	0·89

It will be observed that the ratio CO_2/O is distinctly less than unity and remains practically constant throughout the whole period of vegetation.

The composition of the organic portion of the crop shows that it contains more hydrogen than would form water with the oxygen which it also contains. It seems, therefore, that the plant itself eliminates oxygen in some form, and possibly, as suggested by Dehérain and Maquenne in a similar case, it is eliminated as carbonic anhydride.

On the other hand, the composition of the plant, when compared with the measurements of carbonic anhydride and oxygen, shows that it has derived some oxygen through its roots from the oxy-salts present in the soil. C. H. B.

Supposed Presence of Albumin in the Walls of Vegetable Cells. By S. L. M. Moore (*Chem. Centr.*, 1892, ii, 872—873; from *J. Linn. Soc.*, **29**, 241).—The substance in the cell walls which gives the reactions for albumin is not albumin, at least not a peptonisable albumin, neither is it tyrosine. Krasser's list of the substances which

react like proteïds is not complete, as the three reactions which the cell walls give (Millon's, Raspail's, the xanthroproteïn reaction) are also given by a solution of catechu, as are other reactions shown by the cell walls. The behaviour of lignified cell walls to some reagents shows the presence of an iron-greening dye (probably a tannin) in them. The fact that the cell walls are not able to take up carmine and aniline-blue is not reconcilable with their containing albumin, but no form of tannin takes up carmine, and iron-greening tannins are not coloured by aniline-blue. The cell nucleus also probably contains an iron-greening tannin.

It is doubtful whether proteïds occur in the milky juice of the fig, as the proteïd reactions which this gives may also be due to an iron-greening tannin. A. J. G.

Cork and Suberin. By C. Van Wisselingh (*Chem. Centr.*, 1892, ii, 516; from *Nederl. Tijdschr. Pharm. Chem. Toxicol.*, 1892, 220).—Cork does not contain cellulose. The violet coloration which it gives with zinc chloride and iodine solution is due to phellonic acid. Cork contains several fusible substances, which are soluble in chloroform; these consist of glyceryl salts of the various acids. From the saponification products of these substances, *phellonic acid*, melting at 95°, a second acid melting at 60—70°, and several other less well characterised acids were obtained. The fusible substances mentioned above are enveloped in others which are not fusible or soluble in chloroform, but dissolve readily in cold aqueous potash. A. J. G.

Ethyl Alcohol in Oil of Roses. By T. Poleck (*Ber.*, **26**, 38—39).—Oil prepared in Germany, on the spot where the roses were grown, was found to contain no ethyl alcohol. That previously found in other samples must have been formed by fermentation taking place in the leaves during their transport to the factory. C. F. B.

Occurrence of Thymol in the Ethereal Oil of Mosula Japonica. By Y. Shimoyama and H. Ono (*Chem. Centr.*, 1892, ii, 618; from *Apoth. Zeit.*, **7**, 439—440).—Dried plants of the Japanese labiate *Mosula Japonica*, on distillation with water, yielded 2·13 per cent. of a brownish-red, ethereal oil of feeble, thymol-like odour; it was lævorotatory, and had a sp. gr. = 0·820 at 17·5°. On agitation with strong aqueous soda, an oily liquid boiling at 170—180°, and smelling like cymene, was obtained, whilst the aqueous solution, when saturated with carbonic anhydride, yielded thymol.

A. J. G.

Loss of Nitrogen in Manures. By A. Muntz and A. C. Girard (*Compt. rend.*, **115**, 1318—1321).—The authors have estimated the loss of nitrogen that takes place in the stable before the manure is put into a heap, by estimating the nitrogen introduced in the forage and the litter, also that found in the products, such as milk, wool, &c., and in the manure at the time that it was removed. The difference is taken as the loss of nitrogen occurring in the stable. The results were as follows:—

	16 horses. kilos.	10 cows. kilos.	25 sheep. kilos.
Nitrogen in the forage.....	43·795	90·116	14·548
„ in the litter (straw)..	8·642	6·532	0·115
„ in the animal products	0·000	17·742	0·900
„ in the manure.....	39·860	50·108	6·464
„ lost.....	12·577	28·798	7·299
„ lost per cent. of nitrogen supplied.....	28·7	31·9	50·2

When the manure is in a heap and is left to itself, the losses are much smaller; with horse manure, after four months, the loss is 23·1 per cent. of the initial nitrogen, and 20·9 per cent. of the nitrogen consumed in the fodder; with cows' manure, after three months, 2·39 per cent. of the initial nitrogen, and 10·8 per cent. of the nitrogen consumed in the fodder; and with sheep's manure, after six months, the loss is 11·3 per cent. on the first basis, and 5·0 per cent. on the second.

The relatively great loss of nitrogen in the stable is attributable to the rapid fermentation of the urine; the solid excreta retain their nitrogen longer. The loss is somewhat greater in summer than in winter; in the case of cows, the loss is 52·7 per cent. of the original nitrogen in June and July, and only 44·7 per cent. in January, February, and March. The loss is slightly less when the fodder is green than when it is dry, probably because in the first case the excreta contain more moisture, and the tension of the ammonia is lower. It is not affected to any important extent by increasing the bulk of the litter. C. H. B.

Fermentation of Manure. By A. Hébert (*Compt. rend.*, **115**, 1321—1323).—The author has investigated the changes which the nitrogen undergoes during the fermentation of straw at 55° in the absence of excess of oxygen. The straw was powdered, moistened with 5 per cent. solutions of potassium and ammonium carbonates, and inoculated with a small quantity of liquid manure. Methane and carbonic anhydride were given off, and after three months the straw had lost nearly half its weight. In all cases, there was a reduction in the ammoniacal nitrogen, and an increase in the organic nitrogen, as in Dehérain's experiments. The total loss of nitrogen is considerable, but neither in the experimental flasks nor in the case of manure heaps does this loss take place in the form of ammonia. If a manure is too dry, the methane fermentation is greatly retarded, and it follows that moistening the manure not only promotes this fermentation, but reduces the risk of loss of ammonia.

The nitrogen which is lost escapes in the free state, and hence the practice of adding iron sulphate, calcium sulphate, &c., with a view to prevent loss of ammonia, is useless if the manure is kept sufficiently moist. C. H. B.

Analytical Chemistry.

Quantitative Separation and Estimation of Chlorine, Bromine, and Iodine. By C. FRIEDHEIM and R. J. MEYER (*Zeit. anorg. Chem.*, **1**, 407—422).—After a critical examination of the various methods that have been proposed for the estimation of mixed chlorides, bromides, and iodides, the authors have adopted the following process. The mixture is introduced into a small retort of special form and mixed with potassium dihydrogen arsenate and dilute sulphuric acid. The iodine separates, and can be distilled over into a receiver containing potassium iodide solution, preferably by means of a current of steam. It is then titrated in the ordinary way with thiosulphate solution. The residue in the retort is allowed to cool, and then mixed with a concentrated solution of potassium dichromate. On heating, the whole of the bromine is liberated, and is collected in the receiver, which has been again charged with potassium iodide solution. The iodine set free is determined as before with thiosulphate solution. The chloride which remains in the retort with the excess of dichromate is determined gravimetrically by precipitation with silver nitrate, after the solution has been acidified with nitric acid. The test analyses show that the method gives very fair results. H. C.

Direct Quantitative Separation of Chlorine and Iodine. By P. JANNASCH and K. ASCHOFF (*Zeit. anorg. Chem.*, **1**, 248—250).—The method depends on the insolubility of thallium iodide in aqueous alcohol, and the solubility of thallium chloride in solutions of ammonium salts. About 0·5 gram of a mixture of sodium chloride and iodide is dissolved in 40—50 c.c. of water, and 50 c.c. of 20 per cent. ammonium sulphate solution and 30 c.c. of alcohol added. An excess of 4 per cent. thallium sulphate solution is then introduced, and the mixture allowed to remain in the cold for 12 hours; the precipitated thallium iodide is then collected on a tared filter, washed with a 5 per cent. solution of ammonium sulphate in 30 per cent. alcohol, and finally with 30—50 per cent. alcohol, and, after drying at 100°, weighed. The alcohol is evaporated from the filtrate, and the residue made up to 300 c.c. with water; 10 c.c. of concentrated nitric acid, and the necessary quantity of silver nitrate are then added to the boiling liquid, and the silver chloride collected and weighed as usual. It does not seem possible to separate chlorine and bromine by this method. A. R. L.

Detection of Iodates in Iodides. By F. ROBINEAU and G. ROLLIN (*J. Pharm.* [5], **26**, 485—490).—The authors show that in presence of air and moisture all the acids, even carbonic anhydride, decompose potassium iodide, and that this salt is also decomposed when moist in presence of air and light, but is unaffected in the dark,

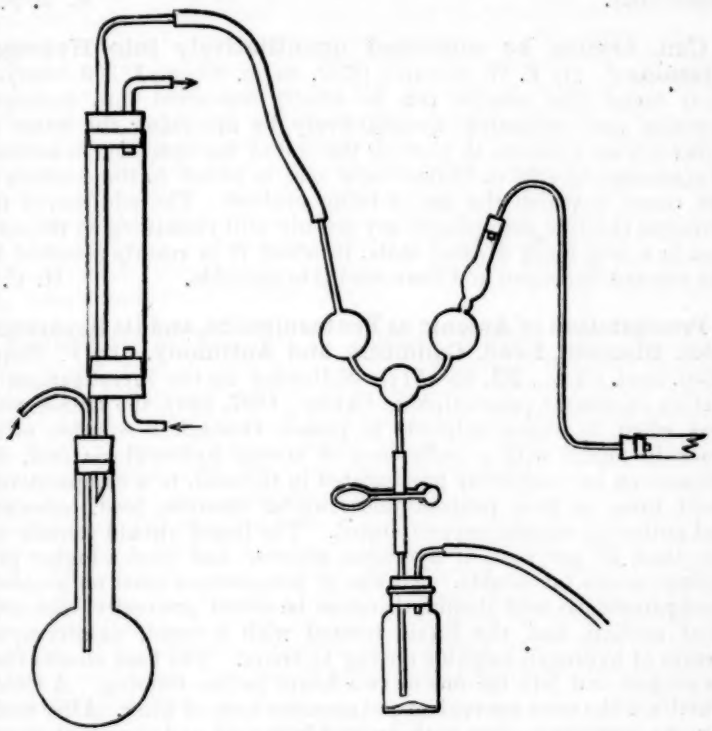
or when the air is replaced by carbonic anhydride or nitrogen; similar results are obtained with solutions of the salt, iodine being set free, whilst the solution becomes alkaline, according to the equation $2KI + O + H_2O = 2KHO + I_2$. The inverse reaction obtains when the moist salt or its solutions are placed in the dark. Consequently they suggest that for the detection of iodates in potassium iodide, an 8 per cent. solution of the salt should be treated with a few drops of hydrogen tartrate solution and starch paste, the immediate coloration being taken as positive evidence of their presence. T. G. N.

Estimation of Nitrogen in Nitrocellulose. By E. v. KEUSSLER (*Zeit. anal. Chem.*, **32**, 51—53).—The following mode of carrying out the treatment with sulphuric acid and mercury (Crum's method; see Abstr., 1887, 86) is both convenient and rapid. A Hofmann's eudiometer, with a small funnel above the stopcock, is used. The nitrocellulose (0·15 gram), wrapped in cigarette paper, is passed round the bend of the tube into the closed limb. The apparatus is then filled with mercury, and by alternately raising and lowering the level of the mercury in the pressure limb, the air is, as far as possible, removed from the cartridge. About 5 c.c. of concentrated sulphuric acid is then introduced through the funnel, and any air, disengaged by its contact with the substance, is expelled. After waiting 10 minutes for the nitrocellulose to dissolve, the tube is held so as to press the palm of the right hand against the open end, and the thumb against the stopcock, and whilst keeping the tube vertical the mercury is thrown up into the acid in the usual manner, as long as nitric oxide is evolved. The gas is measured in the same tube. M. J. S.

Estimation of Nitrogen in Organic Nitrates. By P. RUBTZOFF (*J. Russ. Chem. Soc.*, **23**, 382—388).—The apparatus used by the author to estimate the nitrogen in such substances as nitroglycerol consists of a round-bottomed flask of 150 c.c. capacity, into which are introduced about 25 grams of crystallised ferrous sulphate, 70 c.c. of hydrochloric acid of sp. gr. 1·12, and 0·3—0·5 gram of the substance to be analysed. Connected with the tube passing through the condenser is a Y-shaped bulb tube, into which an almost saturated solution of potassium carbonate can be forced up from the bottle below, so as to fill the lower bulb, and also the side bulbs to about a fourth of their volume. The wide tube sealed on to the last bulb contains solid potassium hydrogen carbonate, and is connected by means of a glass tube with a combustion tube, 40 cm. long and 12 mm. wide, containing a spiral of copper wire gauze, 25—30 cm. long. The other end of the combustion tube is attached to a Schiff's nitrogen apparatus.

Carbonic anhydride is passed into the flask and through the whole apparatus (which has previously been tested to see that it is air-tight), in order to expel the air. The level of the potassium carbonate solution should at this period just reach the lower bulb, so that the apparatus may not become choked up by the deposition of crystals of

potassium hydrogen carbonate. When the air has been completely driven out, the tube containing the copper is heated in a combustion furnace, and the solution of potassium carbonate introduced into the bulbs. The flask is now heated and occasionally shaken, so that a regular stream of gas comes off. The gas is nitric oxide mixed with the vapour of water and hydrochloric acid, the last two being absorbed by



the solution in the bulb tube and by the dry potassium hydrogen carbonate. After three-quarters of an hour, the black, opaque solution in the flask has become reddish-brown and transparent, and very little gas rises in the nitrogen apparatus. The boiling is continued for 10—15 minutes longer, after which the flame is lowered, and carbonic anhydride passed for about half an hour, to sweep out the last traces of gas. The nitrogen apparatus is then disconnected, and the volume read off after cooling.

The results obtained by the author are good: for example, the percentage amount of nitrogen found in trinitroglycerol was 18·36, 18·55, and 18·48; the calculated being 18·50. J. W.

A Source of Error in the Estimation of Phosphoric acid by Magnesia Mixture. By N. v. Lorenz (*Zeit. anal. Chem.*, **32**, 64—67).—In the absence of citric acid, the simultaneous precipitation of some

magnesia (about 1 per cent.) cannot be prevented, even by adding the magnesia mixture drop by drop. When 2 per cent. of citric acid (in the form of the usual ammonium citrate solution) is added, and then the magnesia mixture, drop by drop, not a trace of magnesia can be found in the precipitate, and, with larger proportions of the citrate solution, the slow addition of the magnesia mixture is quite superfluous. M. J. S.

Can Arsenic be converted quantitatively into Hydrogen Arsenide? By F. W. Schmidt (*Zeit. anorg. Chem.*, **1**, 353—359).—It is found that arsenic can be wholly converted into hydrogen arsenide and estimated quantitatively by absorbing the latter in silver nitrate solution, if, towards the end of the operation, a solution of stannous chloride in hydrochloric acid is added to the contents of the vessel in which the gas is being evolved. The addition of the stannous chloride precipitates any arsenic still remaining in the solution in a very finely divided state, in which it is readily attacked by the nascent hydrogen and converted into arsenide. H. C.

Precipitation of Arsenic as Pentasulphide, and its Separation from Bismuth, Lead, Cadmium, and Antimony. By F. Neher (*Zeit. anal. Chem.*, **32**, 45—51).—Following up the investigations of McCay on arsenic pentasulphide (Abstr., 1887, 213), the author finds that when hydrogen sulphide is passed through a solution of an arsenate mixed with a sufficiency of strong hydrochloric acid, the arsenic can be completely precipitated in the cold, in a comparatively short time, as pure pentasulphide, whilst bismuth, lead, cadmium, and antimony remain unprecipitated. The liquid should contain not less than 29 per cent. of hydrogen chloride, and even a higher percentage seems favourable. All rise of temperature must be avoided; the hydrochloric acid should therefore be added gradually, with artificial cooling, and the liquid treated with a rapid, uninterrupted stream of hydrogen sulphide during 1½ hours. The flask should then be corked and left for one or two hours before filtering. A Gooch crucible is the most convenient and accurate form of filter. After washing the precipitate, first with hydrochloric acid and then with water, until free from acid, a trace of free sulphur should be removed by repeated washings with hot alcohol. The precipitate is dried at 100° until constant; it is anhydrous. The reported test analyses, with quantities varying from 0·1 to 0·3 gram, show no error greater than 0·3 milligram. M. J. S.

Methods of Estimating the Sulphur in Sulphides. By L. P. Marchlewski (*Zeit. anal. Chem.*, **32**, 1—45).—The sulphur may either be oxidised to sulphuric acid, or estimated by a direct method. Oxidation by aqua regia, by potassium chlorate and hydrochloric or nitric acid, or by fuming nitric acid alone, gives good results; so also do oxidation with permanganate, and the dry method of Fresenius, both of which, however, occupy much time. Oxidation by chlorine or bromine in alkaline solution, or by hydrogen peroxide, is incomplete. If the sulphuric acid formed is estimated volumetrically, a

saving of time over the gravimetric method can be effected. The alkalimetric methods of Baumann, Clemm, Wilsing, Gawalovski, Knöfler, and Bohlig are of insufficient accuracy; Andrews' method (Abstr., 1890, 414), on the contrary, is exact and rapid.

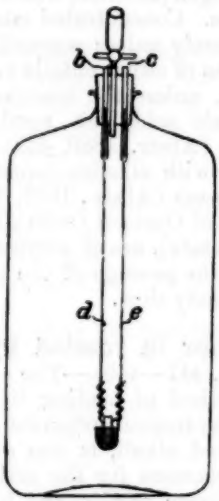
If the sulphur is expelled, in the form of hydrogen sulphide, by hydrochloric acid, it may be accurately estimated by passing it through ammoniacal hydrogen peroxide, which oxidises it to sulphate, or through standard iodine. Concentrated nitric acid does not oxidise hydrogen sulphide completely unless warmed to 80°; aqua regia is more energetic, but the use of either entails complications. Permanganate may be used, but, unless the manganese is removed before precipitating the sulphuric acid, the results are too high. De Koninck's second method (Abstr., 1889, 437) is both convenient and accurate. Weil's method with alkaline copper solution is not trustworthy. Von Berg's process (Abstr., 1887, 301) gives good results. The colorimetric methods of Osmond (with silver nitrate), and Hardy and Arnold (with lead acetate), are of service in some cases, such as the analysis of irons, but the passage of the gas through the absorbing vessels must be extremely slow. M. J. S.

Estimation of Sulphur in roasted Pyrites. By G. Lunge (*Zeit. angw. Chem.*, 1892, 447—449).—The author has long ago concluded that Watson's method of heating the burnt pyrites with a known weight of sodium hydrogen carbonate, and afterwards titrating the excess of undecomposed alkali, is one of the quickest, simplest, and most trustworthy processes for the estimation of the sulphur. But, in order to get accurate results, the following details must be adhered to:—The mixture must be heated for 10 minutes at a temperature just high enough to convert the acid carbonate into the normal salt. The crucible must now be covered, and then heated strongly for 15 minutes, but the temperature must not be high enough to fuse the mass. On no account should the mixture be stirred during the ignition. The mass when treated with boiling water often refuses to give a clear filtrate, but this inconvenience may be avoided by adding some strong brine. L. de K.

Estimation of Sulphur in Coals and Organic Substances. By W. Hempel (*Zeit. angw. Chem.*, 1892, 393—394).—Berthelot having successfully estimated organic sulphur by simply burning the substance in a shell containing oxygen, the author has repeated the process, but with a much simpler apparatus. The substance to be analysed is pressed into a little platinum wire cylinder to which a longish platinum wire is attached.

The combustion is effected in an ordinary glass bottle of about 10 litres capacity (see illustration), which is fitted with a trebly perforated india-rubber stopper. Through this passes a tube with a glass stopcock, the outer end of which widens into a cylinder of about 50 c.c. capacity; also two glass tubes, to the lower ends of which are fused two long, 0·6 mm. thick, platinum wires. One of these wires carries at its lower end a little platinum basket made by folding a piece of platinum wire gauze. When lowered, this basket should be

at a distance of about 25 cm. from the bottom of the flask. For the purpose of electric firing, a little mercury is poured into the tubes *b* and *c*, so as to establish a sure contact with the wires of a 6-cell battery. To carry on an experiment, the india-rubber stopper is removed from the flask, the cylinder containing the substance is put into the basket, and its wire is twisted round the wires *d* and *e* in



such a manner that the electric current is obliged to pass through it. The flask is now filled with distilled water, closed with an ordinary stopper, and placed, inverted, in a porcelain dish containing a little water. After removing the stopper, the flask is filled with oxygen, most conveniently delivered from a cylinder containing the compressed gas. When the flask is filled, the stopper is again put in, the flask is removed from the dish, and put into its normal position. After carefully removing the stopper, the rubber stopper, with its fittings, is inserted. As oxygen is somewhat heavier than air, there is but very little loss of this gas during the operation. The rubber stopper is now firmly tied down with wire, and the substance fired.

After cooling, a mixture of 100 c.c. of water, 5 c.c. of hydrochloric acid, and a little drop of bromine is introduced into the flask by means of the stopcock. After standing for about an hour, or at all events until there is no longer any cloudy appearance, the contents of the flask are washed into a beaker, filtered if necessary, and precipitated with barium chloride. The test analyses are very satisfactory.

L. DE K.

Volumetric Estimation of Sulphuric acid in Sulphates. By E. STOLLE (*Zeit. angw. Chem.*, 1892, 234—235).—The process proposed by the author is based on the following reactions:—Barium chromate dissolves in hydrochloric acid, with formation of barium

chloride and barium dichromate, and from this solution the barium chromate is completely reprecipitated on adding ammonia. If, now, the solution of a sulphate is mixed with a hydrochloric acid solution of barium chromate, the whole of the sulphuric acid is thrown down as barium sulphate. If the liquid is now neutralised with ammonia, the remaining barium is precipitated as chromate, and the chromic acid still remaining in solution therefore serves as a measure of the amount of the sulphuric acid. The actual process is as follows:—A weighed quantity of the substance is dissolved in a 500 c.c. flask, and the solution of barium chromate is added, best from a burette, until the sulphuric acid seems completely precipitated. After adding a slight excess of ammonia, the whole is made up to the mark, filtered, and the chromic acid estimated in an aliquot part of the liquid by means of ferrous sulphate in the usual manner. The test analyses are very satisfactory. L. DE K.

Estimation of Sulphurous Acid in Wine. By M. RIPPER (*J. pr. Chem.* [2], **46**, 428—473).—As a standard method for the estimation of sulphurous acid in wines, the author employs that proposed by Haas (Abstr., 1882, 773), care being taken that the traces of hydrogen sulphide and oxygen, with which carbonic anhydride made from marble and hydrochloric acid are contaminated (compare Pfordten, Abstr., 1885, 836), are removed by washing with potassium permanganate and chromous chloride, and that the ignited barium sulphate (in which form the sulphurous acid is finally weighed) is freed from barium sulphide and chloride by successive treatment with bromine water and hydrochloric acid. This method is far too lengthy for general use as an analytical process, and may be successfully substituted by the following:—50 c.c. of the wine is pipetted into a distillation apparatus full of hydrogen, and 5 c.c. of sulphuric acid (1 : 3) is added; the flask is heated in a glycerol bath at 80—85° for three-quarters of an hour, a current of hydrogen being passed through the apparatus. The evolved sulphurous anhydride is absorbed in a flask containing 20 c.c. of normal potassium hydroxide, through which the hydrogen bubbles, and which, after the time stated, is acidified with 10 c.c. of sulphuric acid (1 : 3), and titrated with *N*/50 iodine solution, starch being used as an indicator.

As a still more rapid method, the author recommends direct titration of the wine with iodine solution; this is only applicable to white wines, or to those whose colour after dilution is sufficiently pale to admit of the recognition of the iodine starch blue; red wines must be treated by the distillation method, if it be necessary to make a determination of the sulphurous anhydride in them; but, inasmuch as their colour does not admit of their being sulphured, this is seldom necessary.

While this method was being investigated, it was noted that the sulphurous anhydride in wine does not exist entirely, or even chiefly, in the form of sulphurous acid or alkaline sulphites, as heretofore supposed; after numerous experiments, detailed in the paper, the conclusion was drawn that the wine contains aldehyde sulphite (compare Boessneck, Abstr., 1888, 942). By direct titration of the wine,

it is possible to determine the "free" sulphurous acid (that existing as sulphurous acid and sulphites) and the "total" sulphurous acid, the difference between the two being the "aldehyde" sulphurous acid.

50 c.c. of wine from the freshly opened bottle is pipetted into a 100 c.c. flask, which has been swept out with carbonic anhydride; 5 c.c. of dilute sulphuric acid (1 : 3), and some starch solution are added, and *N*/50 iodine solution is run in with continual shaking, until the blue colour is permanent for some little time. The end reaction is very distinct, but after some minutes the tannin, &c., in the wine will begin to absorb iodine, and the colour will be again bleached. This titration serves for the estimation of the "free" sulphurous acid. Inasmuch as the "aldehyde" sulphurous acid is not oxidised, at all events for some time, by iodine in presence of sulphuric acid, it must be decomposed by alkali before the total sulphurous acid can be determined. For this purpose, 50 c.c. of the wine is pipetted into a 200 c.c. flask, containing 25 c.c. of normal potash solution, care being taken that the nose of the pipette is beneath the surface of the liquid. After 10—15 minutes, 10 c.c. of sulphuric acid (1 : 3) and some starch are added, and titration with *N*/50 iodine solution effected as before.

Some experiments are quoted to show that the "free" sulphurous acid in wine slowly becomes converted into "aldehyde" sulphurous acid, and that the total sulphurous acid decreases with the age of the wine. A. G. B.

Estimation of Potassium as Perchlorate. By W. Wense (*Zeit. angw. Chem.*, 1892, 233—234).—The author (compare this vol., ii, 46) has proved that by adding a small quantity of perchloric acid to alcohol, the potassium perchlorate becomes practically insoluble therein, and may be very accurately estimated in this manner.

If, when estimating potassium in carnallite, the operator wishes to obviate the removal of sulphates, the following modification of the process is recommended:—The solution is evaporated with perchloric acid to decompose the chlorides, the residue is extracted with acid alcohol, and finally dissolved in hot water. This solution is evaporated in a platinum dish, the residue calcined to convert the perchlorate into chloride, then dissolved in water, and titrated with a standard solution of silver nitrate. L. de K.

Analysis of Hydrogen Alkali Carbonates. By Vizern (*J. Pharm.* [5], **26**, 385; compare Abstr., 1892, 1130).—The total alkali present is first determined by normal sulphuric acid solution; another portion of the salt is converted into normal carbonate by the addition of an alcoholic solution of an alkali hydroxide, and the resulting solution is divided; in the one half, the alkali present is determined by normal sulphuric acid directly, and in the other, after decomposition of the carbonate by means of barium chloride solution. From the results, a formula can easily be deduced to determine the normal carbonate present as an impurity. T. G. N.

Estimation of Soda in Soap. By W. H. Low (*J. Anal. Chem.*, **6**, 423—431).—A few grams of soap is treated with 50—100 c.c. of neutral alcohol, heated to boiling, and standard hydrochloric acid, in excess of the quantity necessary for the decomposition of the carbonate, run in; the carbonic anhydride is expelled by strong ebullition, phenolphthaleïn added, and the liquid titrated with standard soda. The soda unites with the fatty acids, and a neutral soap solution is obtained. The difference between the hydrochloric acid taken and the acid equivalent of the alkali employed gives the amount of sodium carbonate. Blue lacmoïd solution is added, and the liquid titrated with standard hydrochloric acid. As the colour changes to reddish before all the combined alkali is neutralised by the hydrochloric acid, the addition of the acid must be continued until a pure, bright red coloration is obtained which is not altered by the further addition of another drop of acid. The end reaction is quite distinct, even with dark-coloured soaps, but with these the indicator must be freely used.

To determine the amount of the fatty acids, where the molecular weight is not known, the solution is again made alkaline, evaporated to dryness, taken up with water, and the fatty acids separated by the addition of excess of hydrochloric acid; the mixture is then cooled, the separated acids collected, washed with water, and the water removed mechanically as far as possible; the acids are now washed into a flask with hot alcohol, and titrated with alcoholic soda free from carbonate, phenolphthaleïn being used as indicator; finally the solution is evaporated to dryness and the residue weighed. The difference between the weight and that of the soda employed gives the amount of the fatty anhydrides more accurately than the direct weighing of the fatty acids, as in the latter case loss and anhydride formation occur during the drying. If soluble fatty acids are present, the filtrate from the insoluble fatty acids is shaken with ether, the ethereal extract mixed with alcohol, neutralised with alcoholic soda, using phenolphthaleïn as indicator, evaporated to dryness, and the residue weighed. A. J. G.

Electrolysis of Metallic Formates. By H. S. Warwick (*Zeit. anorg. Chem.*, **1**, 285—312).—After giving details of the electrolysis of certain formates, the author sums up his results as follows:—The weight of copper, cadmium, or zinc precipitated in a given time is proportional to the strength of the salt solution; the presence of a moderate amount of free acid exerts no essential influence on the result. By augmenting the distance between the poles, the quantity of metal precipitated is decreased, although the diminution becomes less as the distance between the electrodes increases. Rise of temperature causes an increase in the quantity of metal precipitated, the maximum amount being obtained at 80° with neutral and acid solutions of the copper salts, and at 60° with acid solutions of the cadmium salt. The amount of zinc precipitated in solutions containing free acid decreases, however, with the rise of temperature. Attempts to produce compact coherent deposits of cadmium and zinc in neutral solutions of their formates were unsuccessful; copper and cadmium

are, however, completely precipitated in acid solution, as is also zinc, but the precipitated metal is, in the last case, spongy. Lead separates, chiefly at the cathode, both from acid and neutral solutions; manganese is precipitated at both poles, but the quantity of peroxide which separates at the cathode is, on addition of free acid, reduced to mere traces. The following separations may be satisfactorily effected:—Copper from zinc, cobalt from nickel, and cadmium from zinc and manganese. It was found impossible to precipitate copper in the presence of iron or cadmium, as also zinc in the presence of iron, cobalt, or nickel; it also seems impossible to estimate cadmium in the presence of iron, nickel, or cobalt. A. R. L.

Separation of the Metals precipitated by Hydrogen Sulphide in Acid Solutions. By U. Antony and L. Niccoli (*Gazzetta*, **22**, ii, 408—417).—The metals precipitated by hydrogen sulphide from acid solutions may be divided into three sub-groups, as follows:—1. Antimony, tin, bismuth, cadmium, and lead, whose sulphides are soluble in hydrochloric acid. 2. Arsenic and copper, whose sulphides, although insoluble in hydrochloric acid, are dissolved by nitric acid. 3. Mercury, platinum, and gold, the sulphides of which are not decomposed by either hydrochloric or nitric acid. This classification forms the basis of a scheme which possesses many advantages over other methods employed for separating the above metals.

The precipitate obtained with hydrogen sulphide in the acid solution is washed until the washings are no longer acid, then treated with hydrochloric acid (sp. gr, 1·1), boiled, and the liquid decanted through a filter; the residue is again boiled with hydrochloric acid, first adding a little hydrogen sulphide solution, and is finally decanted through a second filter, the filtrates being then united. During the above treatment, contact with the air is to be avoided, as copper sulphide readily oxidises and dissolves. The residue insoluble in hydrochloric acid is washed on a filter, first with cold, then with hot, water, until the filtrate gives no precipitate with silver nitrate; any lead chloride formed is precipitated as chromate from the hot water washings.

The residue on the filter is then twice boiled with nitric acid (sp. gr. 1·2), decanting the liquid through a filter and uniting the filtrates. The insoluble residue is washed on a filter, when any silver chloride formed by the action of hydrochloric acid on the sulphide can be detected by dissolving it in ammonia; the residue is finally washed well, and dried at 100°.

The hydrochloric acid solution is evaporated to dryness on the water-bath, the residue moistened with ammonia solution, stirred with yellow ammonium sulphide solution, and heated below the boiling point for a short time. On filtering the cooled solution, the antimony and tin are contained in the filtrate, whilst bismuth, cadmium, and lead sulphides remain undissolved. If both cadmium and antimony are present, cadmium sulphantimonate may be formed, but as this decomposes on heating, the residue should be boiled with ammonium sulphide, filtered, and the two filtrates united; the presence of antimony in the solution is betrayed by the characteristic orange-red colour

of its sulphide, obtained on evaporating a little of the solution to dryness on the water-bath. As, however, the colour may be masked by that of free sulphur or stannic sulphide, the residue is dissolved by warming with a few drops of hydrochloric acid on platinum foil; the characteristic black stain due to reduced antimony is then obtained on adding a fragment of zinc. The remainder of the filtrate is now acidified with hydrochloric acid, warmed, the solution decanted, and the precipitate dissolved by boiling with concentrated hydrochloric acid; the solution is then boiled with metallic antimony to convert the tin into stannous chloride. On cooling, filtering, and adding a few drops of saturated mercuric chloride solution, mercurous chloride separates if the solution contains more than 0·01 per cent. of tin.

The residue insoluble in ammonium sulphide may contain bismuth, lead, and cadmium; it is dissolved in the minimum quantity of nitric acid, the solution filtered, excess of ammonia added, and again filtered. Cadmium is precipitated from the filtrate by hydrogen sulphide; the residue is washed, boiled with sulphuric acid (sp. gr. 1·11), and the solution filtered. The filtrate contains the bismuth, which gives the hydrate on adding ammonia, and black bismuthous oxide on pouring into alkaline potassium stannite solution. The residue undissolved by sulphuric acid is lead sulphate, and is identified in the usual way.

The nitric acid extract of the mixed sulphides may contain arsenic and copper, the detection of which presents no difficulties.

The dried residue insoluble in nitric and hydrochloric acids may contain mercury, platinum, and gold; it is heated in the Bunsen flame, in a narrow glass tube closed with cotton wool. Mercuric sulphide sublimes, giving the characteristic black ring, which is readily distinguished from the more volatile sublimate of sulphur due to the decomposition of platinic or auric sulphide. The residue which resists sublimation is removed and heated strongly, to obtain the metals, which are then dissolved in chlorine water or nitrohydrochloric acid, and the solution evaporated to dryness on the water-bath; the aqueous solution of the residue is boiled with oxalic acid, when the gold is deposited as such. The platinum remains in solution, and may be separated as ammonium platinochloride if the usual precautions are taken. W. J. P.

New Method for the Titration of Ferric Salts. By H. Moraht (*Zeit. anorg. Chem.*, **1**, 211—216).—This method consists in titrating a solution of a ferric salt with a standard solution of potassium ferrocyanide, employing potassium thiocyanate as indicator, and therefore obviously depends on the constancy of composition of the precipitate—Prussian blue. This has, however, been satisfactorily settled by Classen (Mohr's *Titriermethode*, **6** Aufl., 235; see also Reynolds, Trans., 1887, 644). The solution, in which all the iron must be present as ferric salt (if it be not, it is oxidised, as described below, with potassium chlorate), is introduced into a stoppered flask of 500 c.c. capacity, together with some potassium thiocyanate and about 50 c.c. of ether, when the latter immediately assumes the well-known, deep red colour of ferric thiocyanate. A

standard solution of potassium ferrocyanide is now run in by degrees from a burette, shaking briskly at intervals, until the ethereal layer is colourless, or of a faint rose tint. This test is to be regarded as preliminary. A second is now made as before, but a volume of ferrocyanide solution, a little less than that found in the previous experiment, is added at once to the ferric salt, and, after shaking the mixture, potassium thiocyanate and a sufficient quantity of ether are introduced. On again shaking and allowing to remain, the ethereal layer will be of a faint rose tint; it is decolorised by the further addition of ferrocyanide solution. As the surface of the Prussian blue is slightly violet, the disappearance of colour from the ethereal layer is best observed by looking through it obliquely from below. The ferrocyanide solution may be standardised with potassium permanganate solution, but the final point is difficult to determine exactly. It is therefore preferable in standardising the ferrocyanide solution to employ a weighed quantity of pure iron, which is dissolved in hydrochloric acid with the addition of potassium chlorate, and after boiling off the excess of chlorine, the test is continued as already described. The titration may be performed either in neutral or acid solutions. The test analyses were satisfactory. A. R. L.

Volumetric Estimation of Cobalt. By W. J. Karslake (*J. Anal. Chem.*, **6**, 469—470).—The cobalt is precipitated as potassium cobaltinitrite, the precipitate boiled with aqueous potash until the liquid becomes colourless, filtered, the filtrate treated with permanganate solution until a violet coloration is produced, then slightly supersaturated with sulphuric acid, and an excess of permanganate solution added: it is then strongly acidified, heated to 80°, and the excess of permanganate titrated back with oxalic acid. The amount of cobalt is deduced from the permanganate required to convert the nitrous acid of the salt $K_3Co(NO_2)_6$ into nitric acid.

A. J. G.

Volumetric Estimation of Chromium. By A. Perrault (*Chem. Centr.*, 1892, ii, 807—808; from *Mon. Sci.* [4], **6**, 722—723).—A modification of Carnot's hydrogen peroxide method (Abstr., 1889, 311, 443). Commercial hydrogen peroxide, diluted with 10 times its volume of water, is employed, and its strength determined on each occasion of using as follows:—3 c.c. of a solution of potassium dichromate containing 37 grams per litre is diluted to a litre, 50 c.c. of this (= 0·003774 gram of CrO_3) is neutralised with 10 per cent. ammonia, and 1·5 c.c. of 10 per cent. solution of hydrochloric acid added; to this the hydrogen peroxide solution is added, drop by drop, until further addition causes no blue coloration.

In estimating chromium in the chromic compounds, a dilute solution of the chromium compound is prepared, and ½ litre of the solution heated at 100°; hydrogen peroxide is run in until the grey coloration first produced has completely vanished, ammonia is then added, and the mixture heated for 10 minutes, when the colour, originally green, becomes brown, and finally clear yellow, the solution then containing ammonium chromate. After cooling, it is made up to 500 c.c., and 50 c.c. titrated as above described.

If both chromates and chromic compounds are present, the latter are converted into chromic acid, and the total chromium estimated in one portion, whilst in a second portion the preformed chromic acid is estimated, and the chromic compounds found from the difference between the two titrations. A. J. G.

New Method of estimating Vanadic Oxide. By A. ROSENHEIM and C. FRIEDHEIM (*Zeit. anorg. Chem.*, **1**, 313—317).—The method depends on the gravimetric estimation of the carbonic anhydride which is evolved in accordance with the equation $V_2O_5 + H_2C_2O_4 = V_2O_4 + H_2O + CO_2$, when a solution of vanadic acid is boiled with one of oxalic acid in the presence of sulphuric acid. The results are not affected by the presence of phosphoric, tungstic, or molybdic acid, and the method has an advantage over that of Holverschedt (Abstr., 1890, 1343), in that the base may be estimated in the same portion. For this purpose, the residual solution, after expelling the carbonic anhydride, is evaporated to a syrupy consistence in order to decompose the excess of oxalic acid, oxidised with nitric acid, neutralised with ammonia, and, after removing the acids with mercurous nitrate, the base is determined in the filtrate. A. R. L.

Palladium Compounds. By M. FRENKEL (*Zeit. anorg. Chem.*, **1**, 217—239).—Attempts to prepare hydrogen palladious cyanide by extracting an acidified solution of potassium palladious cyanide with ether were unsuccessful. Potassium palladious cyanide is decomposed on boiling a solution of it with hydrochloric acid. The whole of the palladium is in fact precipitated as palladious cyanide without the use of mercuric cyanide (Fresenius) when potassium cyanide is added to a solution of palladious chloride, and after acidifying the mixture with hydrochloric acid, the hydrogen cyanide is driven off by boiling. The precipitation of silver chloride on adding silver nitrate to solutions of the chlorides of palladium is incomplete, and the precipitate is contaminated with palladium compounds. Accurate results are obtained, however, both in the determination of the metal and halogen, by heating the palladium chloride solution with alcoholic sodium hydroxide on the water bath, collecting, washing, drying, and weighing the precipitated metallic palladium; the chlorine is then estimated in the filtrate as silver chloride after acidifying with nitric acid.

When potassium chromate is added in excess to a solution of palladious chloride, the palladium is quantitatively precipitated as a reddish-brown precipitate, which when heated at 110° has the composition $15PdO,PdCl_2 + 11H_2O$. The latter reaction can be made use of for the estimation of palladium, as the new compound yields metallic palladium on ignition; it may, perhaps, also serve for the separation of palladium from other metals of the platinum group. Palladosoammonium chloride, $PdCl_2,2NH_3$, is precipitated when a solution of ammonium palladious chloride is boiled with potassium chromate. A. R. L.

Estimation of Iron in Spring Water. By F. Gerhard (*Arch. Pharm.*, **230**, 705—710).—The use of tannin (from galls) as a colorimetric reagent is proposed; by its means $\frac{1}{15}$ milligram of iron per litre can be detected. The following solutions are made up; (1) 1 part of crystallised sodium pyrophosphate in 20 parts of water; (2) 1 part of tannin in 20 parts of dilute alcohol; (3) 0·898 gram of iron-alum, and 2·5 grams of crystallised sodium pyrophosphate in 1 litre of water; this contains 0·1 milligram of iron per c.c.

If the water is fresh and still clear, 100 c.c. of it is taken, 20 c.c. of (1) and 5 drops of (2) are added, and the colour is compared with that obtained with a mixture of 100 c.c. of water free from iron with 20 c.c. of (1), 5 drops of (2), and a certain quantity, best 1 c.c., of (3). If the water to be examined already contains a precipitate, it is shaken up, and 150 c.c. are placed in a flask and heated with 1 gram of oxalic acid. To the hot liquid a granule of potassium citrate is added (to prevent precipitation of iron), the solution is saturated with calcium carbonate to remove the oxalic acid, filtered, and treated as above with 20 c.c. of (1) and 5 drops of (2). In this case, the results are not quite so accurate. C. F. B.

Impurities in Crude Methyl Alcohol. By E. Barillot (*Compt. rend.*, **115**, 1315—1317).—When 20 c.c. of chloroform is agitated with a mixture of 10 c.c. of methyl alcohol, 15 c.c. of a solution of sodium hydrogen sulphite of sp. gr. 1·325, and 5 c.c. of water, the coefficient of division between the two non-miscible liquids is such that the chloroform retains its original volume when the methyl alcohol contains no impurity other than acetone. If, on the other hand, the alcohol contains impurities such as benzene, diallyl, &c., the chloroform increases in volume in proportion to the quantity of impurity.

In actual work, the methyl alcohol, sulphite solution, and water are first thoroughly mixed in the proportions given, and the mixture is then agitated with the 20 c.c. of chloroform in a graduated tube, the increase in the volume of the chloroform being read off. The increase in volume in c.c. multiplied by 10 gives the percentage of impurity other than acetone.

At least 10 per cent. of impurities other than acetone must be present if the alcohol is to be effective as a methylator, but many commercial samples of methyl alcohol contain only from 2 to 5 per cent. of such impurities. C. H. B.

Analysis of Explosive Nitro-compounds. By P. G. Sanford (*J. Anal. Chem.*, **6**, 311—318).—In analysing dynamites, the water is estimated directly by exposure for 6—8 days over calcium chloride and the kieselguhr by extracting the nitroglycerol with ether and weighing the residue; the nitroglycerol being calculated from the difference. Blasting gelatins, after estimation of the water as above, are treated with a mixture of ether and alcohol, and the insoluble residue, consisting of wood-meal, nitre or other salts, is collected, dried, and weighed. From the solution, the nitrocellulose is precipitated by the addition of chloroform, collected on a linen filter, redissolved in a mixture of ether and alcohol, reprecipitated, collected, partly dried at 40°, and scraped

off the linen filter; it is then again dried at 40° until constant, and weighed. The nitroglycerol is best estimated by difference, but may be obtained directly by evaporating the filtrate from the nitrocellulose at 30—40° and weighing the residue. In analysing guncotton, the water must be estimated immediately on opening the sample, by drying at 100°; the dried residue is then exposed to the air for two hours, treated with ether-alcohol to remove the soluble pyroxylin, and the insoluble residue, consisting of unchanged cotton and the hexanitrate, collected on a linen filter, dried at 100°, and weighed. The weight of the unchanged (non-nitrated) cotton is obtained by twice boiling a fresh sample with sodium sulphide solution and weighing the insoluble residue. The best test for the purity of guncotton is, however, the determination of the nitrogen, which is best effected by Crum's method, using a Lunge's nitrometer. A. J. G.

Estimation of the Volatile Fatty Acids in Butter Fat. By A. Partheil (*Chem. Centr.*, 1892, ii, 635—636; from *Apoth. Zeit.*, **7**, 435).—5 grams of filtered, dry butter fat is placed in a flask of 300—350 c.c. capacity and 2 c.c. of 50 per cent. aqueous soda and 20 c.c. of glycerol added. The mixture is then carefully boiled over wire gauze until all the water is expelled, the flask being gently rotated the while; the heating is then continued with a smaller flame. After 15—20 minutes, a clear soap solution is obtained, which, after cooling, is mixed with 90 c.c. of water and 50 c.c. of dilute sulphuric acid (50 c.c. of pure acid per litre), some fragments of pumice added, and the mixture distilled until 110 c.c. has passed over. The author regards the method as quicker and more convenient than the older methods, but the test analyses appear to be far from satisfactory. A. J. G.

Baudouin's Test for Sesame Oil. By V. Villavecchia and G. Fabris (*Zeit. angw. Chem.*, 1892, 509—510).—The authors have made a thorough investigation of this test, and propose to apply it as follows:—

0·1 gram of sugar is dissolved in a test tube in 10 c.c. of hydrochloric acid, sp. gr. 1·19. 20 c.c. of the sample of olive oil is then added, the whole thoroughly shaken for a minute, and allowed to settle. If the oil is pure, the acid and oily layers retain their original colour, but if sesame oil is present they are *both* of a decidedly reddish shade. L. de K.

Estimation of Fat in Bread. By M. Weibull (*Zeit. angw. Chem.*, 1892, 450—451).—The author was surprised to find in a sample of bread much less fat than might have been expected considering the nature of the flour used. Prolonged treatment (160 hours) in the Soxhlet tube gave a reasonable percentage of extract, but this was afterwards found to consist mainly of glucose. Fairly accurate results can, however, be obtained as follows:—About 2 grams of the sample is boiled for at least an hour with 30 c.c. of water acidified with sulphuric acid; when the starchy matter has dissolved, the liquid is neutralised with powdered marble, and the mixture is soaked up in blotting paper of the kind employed in Adams' milk

process. After thoroughly drying, the paper is put into a suitable extraction apparatus and extracted with anhydrous ether for about eight hours. L. DE K.

Analysis of Bees-wax by Hübl's Method. By J. A. ANTUSHEVITCH (*J. Russ. Chem. Soc.*, **23**, 223—235).—The author has analysed a large number of waxes both pure and commercial, according to Hübl's method. He finds that heating on a water-bath for three-quarters of an hour with alcoholic potash, as Hübl recommends, is not sufficient to effect the complete saponification of the myristyl palmitates. He heats for four hours over a free flame. The normal ratio of the quantity of potash necessary for saponification to that necessary for neutralisation of the free acid present he fixes at 3·75. The following formula is given for finding the quantity of stearic acid present in wax candles:—

$$x = \frac{284(S - A/3{\cdot}75)}{56{\cdot}1};$$

x is the percentage of stearic acid, S the number of milligrams of potash necessary for the neutralisation of 1 gram of substance, and A the number necessary for saponification of the same quantity.

J. W.

Estimation of Water and of Free Fatty Matter in Soap. By J. A. WILSON (*Chem. News*, **66**, 200).—2·5 grams of the soap, melted in a porcelain dish, and heated on a water-bath with 5 c.c. of absolute alcohol until dissolved, is mixed with 10 grams of ignited sand, and, after exposure on the water-bath for an hour, is treated again with 5 c.c. absolute alcohol; it is then heated to constant weight in an air-oven at 100—105°, which may take from three to six hours, according to the quantity of water in the soap. Moreover, provided the soap does not contain free alkali, the residue may be extracted in a Soxhlet apparatus for fat estimation. D. A. L.

Estimation of Theobromine in Cacao Beans. By P. SÜSS (*Zeit. anal. Chem.*, **32**, 57—63).—The methods of Tuchen, Bell, König, Zipperer, Wolfram, Trojanowski, and Diesing yield widely varying results. In contradiction to Diesing, the author finds that the cacao fat may be extracted by light petroleum without dissolving a trace of theobromine. Diesing extracts the theobromine by chloroform in a Soxhlet's extractor, but the following method gives a much higher yield and seemingly a purer product. The fermented bean is intimately mixed with an equal weight of purified quartz sand, and 6 grams of this mixture is extracted for 10 hours with light petroleum. The residue is boiled for half an hour with 200 c.c. of water and 6 grams of elutriated lead oxide, decolorised, and filtered, the residue being twice more boiled with 100 c.c. of water. The filtrates are evaporated to 10 c.c., introduced into a separator bulb, and shaken for three minutes with 100 c.c. of chloroform, the chloroform solution being run off when perfectly clear (three hours), and the operation repeated twice more. The greater part of the chloroform is distilled off, and the remainder evaporated in a tared beaker, drying the

residue at 100°. From appearance, qualitative tests, ash, and nitrogen estimations, the product seemed to be practically pure theobromine. The yield was nearly double that obtained by Zipperer's method, and 40 per cent. higher than Diesing's, although Diesing's product was brown. M. J. S.

Volumetric Estimation of Alkaloïds. By E. Léger (*Compt. rend.*, **115**, 732).—Referring to the paper by Barthe on the claim for priority made by Harsten (*Compt. rend.*, 1892), the author points out that in 1885 (*J. Phys. Chim.*, **11**, 425) he stated that alkaloïds were neutral to phenolphthaleïn, and that this fact could be utilised in the volumetric analyses of salts of the alkaloïds. C. H. B.

Volumetric Estimation of Alkaloïds. By P. C. Plugge (*Compt. rend.*, **115**, 1012).—A claim for priority against Barthe (this vol., ii, 146). The author described, in 1886, a method of estimating alkaloïds volumetrically, using phenolphthaleïn and litmus as indicators (Abstr., 1887, 621—622). C. H. B.

Analysis of Quinine Sulphate and Estimation of Quinine in presence of other Cinchona Alkaloïds. By L. Barthe (*Compt. rend.*, **115**, 1085—1088).—The author admits that Léger has the prior claim as originator of a volumetric process for the estimation of alkaloïds, based on the use of phenolphthaleïn.

If different weights of commercial quinine sulphate are agitated with a given volume of water at 15—20°, the quantity of decinormal potassium hydroxide required for the saturation of the saturated solutions is greater the greater the quantity of quinine sulphate taken. Moreover, the progressive increase in the quantity of alkali required is in a constant ratio with the weight of quinine sulphate taken. Quantities of 1, 2, 3, 4, and 5 grams of quinine sulphate respectively were agitated frequently with 100 c.c. of water at 20°, and after an hour were filtered. The solutions required respectively 4·6, 5·3, 6·0, 6·7, and 7·4 c.c. of potash solution. The constant difference, 0·7 c.c., represents the quantity of sulphates, other than quinine, present in each gram of the sulphate taken. It is the factor which measures the impurity, and the latter may be calculated to crystallised cinchonidine sulphate (equiv. = 397); then $0·7 \times 100 \times 0·0397 = 2·779$, the percentage of cinchonidine sulphate in the sulphate employed.

The analysis of quinine sulphate can, therefore, be made in the following way:—Two quantities of 1 gram and 5 grams of the salt are each agitated with 100 c.c. of water at 20° for frequent intervals during an hour, filtered, and the filtrate titrated with decinormal potash. The difference between the quantities of alkali required by the two solutions, multiplied by the expression $100 \times 0·0397 \div 4$, gives the percentage of impurity calculated as cinchonidine sulphate.

The solubility of quinine sulphate for a given temperature between 12° and 20°, and even 25°, is sensibly different, according to the conditions under which the solubility is determined. At 12°, 1000 c.c. of water dissolve 1·482 grams of quinine sulphate when the latter is

triturated and agitated with it for about an hour; at 20°, 1000 c.c. dissolve 1·744 grams, but if the liquid is allowed to remain in contact with the excess of dissolved salt, and is frequently agitated, the temperature can be reduced to 12° without any of the salt separating from solution; that is to say, 1000 c.c. contain 1·744 grams of the salt. If, on the contrary, the liquid remains at rest whilst cooling from 20° to 12°, or to 15°, the quantity of salt remaining in solution per litre is 1·482 to 1·787 grams, and is not always the same for the same final temperature. The differences are still greater if the liquid remains at rest for 24 or 48 hours, and the solubility may then be as low as 1·133 and 1·09. The solutions thus obtained are stable *after filtration*, even at temperatures several degrees below the temperature of saturation. They cannot dissolve any more quinine sulphate at the temperature at which they were formed, or at a lower temperature, but they can dissolve 9·92 grams per litre of crystallised cinchonidine sulphate, and 12·42 grams of crystallised cinchonine sulphate.

In order to estimate quinine in cinchona bark, a chloroform solution of the alkaloïds obtained by any of the ordinary methods is vigorously and repeatedly agitated with a measured excess of decinormal sulphuric acid, evaporated until the chloroform is expelled, and the excess of acid estimated by means of standard alkali and litmus. Sufficient sulphuric acid is added to the mixture to redissolve the alkaloïds, which are then reprecipitated by potassium hydroxide, and dissolved in chloroform. The chloroform solution is evaporated just to dryness with the exact quantity of sulphuric acid found in the first titration to be necessary for complete neutralisation. The residue is triturated with 200 c.c. of a solution of pure quinine sulphate saturated at 20°; after two hours' digestion, the liquid is filtered. The filtrate is a saturated solution of quinine sulphate containing the sulphates of the other alkaloïds. 100 c.c. is titrated with potassium hydroxide, using phenolphthaleïn as indicator. Twice the volume of alkali required, *minus* 8 c.c., gives the quantity of impurities, which can be calculated to crystallised cinchonidine sulphate. The result can be controlled by estimating the quantity of quinine sulphate left on the filter. C. H. B.

Chromic Acid as a Reagent for Albumin and Bile Pigments in Urine. By O. Rosenbach (*Chem. Centr.*, 1892, ii, 557; from *Deut. med. Woch.*, 1892, No. 17).—When a few drops of 5 per cent. chromic acid solution is added to feebly acidified urine, the albumin is precipitated in flocks, even if present in but very small quantity. Phosphates and urates do not interfere with the test.

If bile pigments are present, the urine assumes an intense green colour on adding the chromic acid, but it is essential that the chromic acid be added drop by drop with constant agitation, otherwise the liquid becomes brownish-red, and the addition must be made the more carefully the larger the amount of the bile pigments present. A. J. G.

General and Physical Chemistry.

Study of Chemical Reactions in a Liquid Mass by means of the Index of Refraction. By C. FÉRY (*Compt. rend.*, **115**, 1309—1312).—By comparing the indices of refraction of solutions containing two substances which are capable of acting one on the other with those calculated on the assumption that the observed index should be given by the mean of those of the two constituents, it is possible to gain evidence of the occurrence of chemical change in solution. Thus, in a solution containing sodium hydroxide and nitric acid, it was found that the maximum deviation of the observed from the calculated values occurred in a solution containing 8 parts of NaOH and 12·31 parts of HNO_3 in 100 of water, the ratio 12·31/8·00 being nearly equal to that of HNO_3/NaOH. In the case of mixtures of alkalis with sulphuric acid, there are two points at which changes occur in the curve for the indices of refraction, one corresponding with a mixture that would form the acid, and the other to one that would form the normal salt. The curve for phosphoric acid has three such points. In cases where no chemical action occurs, the observed and calculated values for the indices of refraction are found to coincide, the curve for the indices of refraction of such mixtures being a continuous straight line.

In addition to the points where the maximum deviation of the observed from the calculated values occurs, the author has observed certain other slight changes and breaks in the indices of refraction curves. These breaks he attributes to the formation of hydrates by the union of water with the substances under examination. A special study of this point, in the case of sulphuric acid solutions, showed that such breaks occurred with solutions corresponding with the hydrates $H_2SO_4,4H_2O$; $H_2SO_4,2H_2O$; $H_2SO_4,1\frac{1}{2}H_2O$; and H_2SO_4,H_2O.

H. C.

Spectrum of Liquid Oxygen and Refractive Indices of Liquid Oxygen, Nitrous Oxide, and Ethylene. By G. D. LIVEING and J. DEWAR (*Phil. Mag.* [5], **34**, 205—209).—The hot pole of an electric arc was viewed through a column of 3 inches of liquid oxygen with a spectroscope having two calcite prisms of 30° and one of 60°. The red potassium lines were used as reference rays. Instead of the solar A, a band was observed having a sharp edge on the less refrangible side and fading away gradually on the more refrangible side. The sharp edge did not coincide with the sharp edge of A, the wave-length being about λ7660. No band corresponding with B was observed, but through a thickness of 6 inches of liquid oxygen a faint band appeared, which had precisely the same character as A, the wave-length of the sharp edge being λ 6905. Liquid oxygen is distinctly blue, this colour, apparently, not being due to ozone. Ozone explodes at a low temperature with great violence.

The refraction constant, $\frac{\mu_D - 1}{d}$, for oxygen at its boiling point, $-182°$, is 0·1989, and its refraction equivalent 3·182. For the formula $\frac{\mu^2 - 1}{(\mu^2 + 2)d}$ the corresponding values are 0·1265 and 2·024.

For liquid nitrous oxide at $-90°$, $\frac{\mu_D - 1}{d} = 0·2634$ and $\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0·163$, giving the molecular refractions 11·587 and 7·163 respectively. Ethylene gives at $-100°$, $\frac{\mu_D - 1}{d} = 0·627$ and $\frac{\mu_2 - 1}{(\mu_2 + 2)d} = 0·384$. The corresponding numbers for gaseous ethylene are 0·578 and 0·385.

J. W.

Phosphorescent Zinc Sulphide as a Photometric Standard. By C. Henry (*Compt. rend.*, **116**, 98—99).—Within somewhat wide limits, which correspond with luminous saturation, the quantity of light emitted by a surface of phosphorescent zinc sulphide at a given instant is independent of the distance of the exciting magnesium, of the time of illumination, and the thickness of the layer of zinc sulphide.

The law of the loss of luminosity of phosphorescent zinc sulphide is always the same, although the sulphide may have been prepared by different workers at different times, and although the initial intensity of luminosity may not be the same. This law is represented by the expression $i^m(t + c) = K$, the value of m being 0·598 and of c, 28·35. The law holds good also for thicknesses of the layer of sulphide varying from 0·45 mm. to 0·9 mm. Within these limits of thickness the maximum intensity of the phosphorescence is independent of the length of magnesium ribbon burnt and of the distance at which it is held, provided that the length of ribbon is not less than 15 cm. and the distance is not greater than 28 cm.

C. H. B.

Thermoelectric Phenomena between two Electrolytes. By H. Bagard (*Compt. rend.*, **116**, 27—29; compare Abstr., 1892, 1037).—The method previously described has been applied to the investigation of the behaviour of couples formed by two solutions of zinc sulphate of different concentrations. For a given temperature, the electromotive force is greater the greater the difference between the degrees of concentration of the two solutions. The neutral point is also higher the greater the difference of concentration. The *law of intermediate substances* and the *law of intermediate temperatures* were both found to hold good.

C. H. B.

The Ignition Point. By A. Mitscherlich (*Ber.*, **26**, 160—164; compare *Ber.*, **9**, 314).—This paper forms one of a series the author is about to publish on the combustion point and ignition point, the former term denoting the temperature at which combination commences and the latter the temperature at which it takes place with evolution of light; the combustion points of gaseous mixtures will be first dealt with, and afterwards those of liquids and solids. The present

paper gives the results obtained with a mixture of hydrogen and oxygen.

The mixture of these gases was passed through a combustion tube of 4·2 mm. diameter heated in a crucible, the temperature of which was measured by a specially constructed pressure thermometer. The ignition point was found throughout a long series of experiments to be 671°, and is independent of the methods by which the gases are prepared so long as they are pure, of the action of light, of long continued heating if the temperature is below the combination point, and of the motion of the gases. The product of combination formed, if the mixture is only heated somewhat above the combustion point, considerably affects the ignition point, and the mixture must therefore be heated as quickly as possible to the latter temperature.

H. G. C.

Diffusion Phenomena with Precipitate Membranes. By P. WALDEN (*Zeit. physikal. Chem.*, **10**, 699—732).—To obtain membranes suitable for diffusion experiments the following plan was adopted. The tubes taken were about 50 mm. in length and 10 mm. in diameter. After closing the upper end with the thumb, the lower end was dipped into a warm 20 per cent. solution of gelatin, containing ammonium chromate. After carefully draining off the excess of gelatin, a membrane is left closing the end of the tube, which hardens and becomes insoluble on exposure to light. To obtain a precipitate within such a membrane the tube is filled with a solution of one of the precipitants and is then placed in a solution of the other, when they meet by diffusion and form the precipitate in the membrane.

The behaviour of a large number of different precipitate membranes towards salt solutions was examined, the author giving a general record of his results in tabular form. Both electrolytes and non-electrolytes diffuse through precipitate membranes. The acids and salts of monacid bases or monobasic acids diffuse with greatest readiness, salts of polyacid bases or polybasic acids only diffusing slowly and with difficulty or even not at all. The diffusibility of different compounds depends rather on the nature and the arrangement of their components than on the number or weight of the atoms, and is not directly related to the diffusibility of the ions in the case of electrolytes. At the same time, quantitative measurements with salts of the alkali metals show that both the positive and negative ions pass through the membrane in quantities that are in the order of their electrical velocities of transference. The numbers in the case of the free acids are not proportional to their affinity coefficients, although acids having the same affinity coefficients are found to diffuse through the membrane in equivalent quantities. H. C.

Influence of the Concentration of the Ions on the Intensity of Colour of Solutions of Salts in Water. By C. E. LINEBARGER (*Amer. J. Sci.* [3], **44**, 416—418).—As the intensity of the colour of a solution depends in a great measure on the number of ions contained in it, and the electrical conductivity of salt solutions increases as the temperature rises, if a coloured solution is heated, its colour

should deepen. Abundant experimental proof of this is to be found in Gladstone's investigation, "On the Effect of Heat on the Colour of Salts in Solution" (*Phil. Mag.*, **14**, 423). H. C.

Determination of Molecular Weight at the Critical Point. By P. A. GUYE (*Ann. Chim. Phys.* [6], **26**, 97—112).—The substance of this paper has been previously published (compare Abstr., 1891, 1411). F. S. K.

Molecular Dissymmetry. By P. A. GUYE (*Ann. Chim. Phys.* [6], **25**, 145—226).—The author explains at considerable length his views on the nature of molecular dissymmetry, and gives a list of the optically active substances which he has examined (compare Abstr., 1892, 399, 758). F. S. K.

Simplification in the Process of Fractional Distillation. By A. TIGERSTEDT (*Ber.*, **26**, 172).—In order to ascertain the weight of the fractions passing over at different temperatures when the separation of the fractions is not required, the author recommends the placing of the receiver on a small balance such as is frequently employed for letters, in which the weight is shown by means of a pointer and scale. The position of the pointer at the different temperatures is then read off and the weight of each fraction thus ascertained. H. G. C.

Inorganic Chemistry.

Preparation of Pure Iodine. By C. MEINEKE (*Chem. Zeit.*, 1219—1220; 1230—1233).—Musset has recommended the following process:—A suitable quantity of iodine is put into a beaker and covered with a concentrated solution of potassium iodide. Heat is applied until the iodine has fused. After cooling, the cake of iodine is washed, and is then free from chlorine.

The author has improved the process, and has succeeded in also removing any cyanogen. Instead of potassium iodide alone, he prefers a mixture of a solution of calcium chloride (sp. gr. 1·35) and a little potassium iodide, with a few drops of hydrochloric acid. The iodine is then sublimed twice, the first time with the addition of a little barium oxide. Absolutely pure iodine is obtained in this manner. L. DE K.

Physical Constants of Fluorine. By H. MOISSAN (*Ann. Chim. Phys.* [6], **25**, 125).—The author gives a *résumé* of his recent work on the physical constants of fluorine (compare Abstr., 1890, 208, 329); fluorine does not liquefy at −95° under the ordinary atmospheric pressure. F. S. K.

Action of Sulphur in presence of Water on Salts of Polybasic Acids. By J. B. SENDERENS (*Bull. Soc. Chim.* [3], **7**, 511—516).—In a former paper (Abstr., 1892, 770), the author dealt with the action of sulphur in presence of water on salts of monobasic acids. He now states that in the case of nickel and cobalt oxides there is first formed a sulphate and a thiosulphate, but as the reaction proceeds the amount of the latter gradually becomes less until it is reduced to *nil*. He then proceeds to give the results of similar observations on the salts of polybasic acids. Sulphur is without action on boiling solutions of alkali sulphates and oxalates; solutions of bibasic tartrates and tribasic citrates which exhibit alkaline reactions are completely neutralised when boiled with sulphur and water; it is concluded that tartaric acid has a strong acidic function and a medium one, and citric acid two strong acidic functions and a medium one. Carbonates and borates are completely decomposed when boiled with sulphur and water, so that the acidic functions of the corresponding acids are feeble. Tribasic alkali phosphates behave as if they had a function 1·5 times that of a strong acid, and the corresponding calcium and barium derivatives as though they had two strong acidic functions. Tribasic silver phosphate is completely reduced when boiled with sulphur and water, as are likewise the copper salts $Cu_3(PO_4)_2$, $CuHPO_4$, $CuH_4(PO_4)_2$, but the phosphates of lead, nickel, and cobalt remain unaltered. The phosphates, therefore, behave very like the sulphates, and phosphoric acid would seem to have three strong acidic functions. On boiling trisodium arsenate with sulphur and water, it is converted into a thiosulphate and a polysulphide; the latter decomposes with the evolution of hydrogen sulphide, which reacts with the unaltered arsenate, forming thioarsenate and oxythioarsenate. Sodium arsenite gives rise to a polysulphide which decomposes into hydrogen sulphide, forming arsenious sulphide, and finally sodium sulpharsenite. Potassium chromate is thus decomposed:—$6K_2CrO_4 + 15S + 9H_2O = 6Cr(OH)_3 + 5K_2S_2O_3 + K_2S_5$; the polysulphide then decomposes into hydrogen sulphide and potassium thiosulphate. In the case of potassium dichromate, the reaction is as follows:—$7K_2Cr_2O_7 + 10S + Aq = 2(CrO_3,3Cr_2O_3) + 4K_2SO_4 + 3K_2S_2O_3 + Aq$. The *compound* $CrO_3,3Cr_2O_3$ is a brown precipitate. The last-named results are in agreement with the observations of Sabatier (Abstr., 1886, 973). Potassium manganate is thus decomposed:—$2K_2MnO_4 + 5S + 2H_2O = Mn_2O_3,H_2O + 2K_2S_2O_3 + H_2S$ whilst in the case of potassium permanganate, potassium sulphate and manganese dioxide are obtained. A. R. L.

Tellurium. By E. PŘIWOZNIK (*Chem. Centr.*, 1892, ii, 962; from *Österr. Zeit. Berg. Huttenwesen*, **44**, 529—531).—Crude tellurium is fused in a bulb tube of difficultly fusible glass in a stream of hydrogen gas. The hydrogen serves not only for the decomposition of tellurous oxide, which prevents the satisfactory fusion of the tellurium, but also removes any selenium by converting it into hydrogen selenide. Tellurium can also be distilled in a stream of hydrogen, best from a porcelain boat placed in a tube of hard glass; it is deposited

on the cold portion of the tube, partly in lustrous drops, partly in spear-shaped prisms, having numerous striated and hollowed faces. Tellurium has sp. gr. 6·2459 at 18·2°. In determining the sp. gr. it is necessary to boil carefully with water, in order to displace any air from the fine cavities which generally occur in the regulus.

A. J. G.

Nitrous acid in Nitric acid. By L. Marchlewski (*Zeit. anorg. Chem.*, **2**, 18—20; compare Abstr., 1892, 113; and Montemartini, *Real. Accad. Linc.*, 1892, i, 63—67).—The author criticises Montemartini's results, and shows that they do not bear the interpretation the latter puts on them, his method, indeed, being incapable of detecting any but a relatively large quantity of nitrous acid, in the case when nitrogen peroxide is also present. C. F. B.

Action of Hydrogen Arsenide, Antimonide, and Phosphide on Silver Nitrate. By D. Vitali (*L'Orosi*, 1892, 397—411).—The action of hydrogen arsenide on aqueous silver nitrate has been considered by Lassaigne (*J. Chem. Med.*, **16**, 685) to proceed in accordance with the equation $2AsH_3 + 12AgNO_3 + 6H_2O = 12HNO_3 + 6Ag_2 + 2H_3AsO_3$; the reaction, however, occurs in two stages, as follows:—

$$2AsH_3 + 12AgNO_3 = 2(Ag_3As,3AgNO_3) + 6HNO_3,$$
$$2(Ag_3As,3AgNO_3) + 6H_2O = 6HNO_3 + 6Ag_2 + 2H_3AsO_3.$$

Marchlewski (Abstr., 1891, 1154) supposed that any representation of this reaction which involves the simultaneous liberation of silver and nitric acid must be untrue, for he found that dilute nitric acid dissolves finely divided silver; he further stated that arsenious acid reduces dilute nitric acid with formation of nitrous acid, which greatly assists the action of nitric acid on silver. The author, however, finds that on passing hydrogen arsenide into neutral silver nitrate solution, the amount of silver nitrate decomposed and the quantities of free nitric and arsenious acids subsequently remaining in the solution are in the proportions indicated by the above equations; he was unable to detect the presence of nitrous acid. Marchlewski's objections to Lassaigne's equation are therefore invalid, and Houzeau's method for determining arsenic acid, depending on this reaction, is an exact one.

Several chemists have stated that silver nitrate solution is reduced on passing a current of pure hydrogen through it; this the author shows to be due to impurities present in the gas, silver nitrate solution being extremely sensitive to hydrogen arsenide, antimonide, or phosphide.*

The action of hydrogen antimonide on aqueous silver nitrate is in all respects analogous to that of the arsenide; in this case, however, the antimonious acid, being insoluble, separates with the silver, from which it may be extracted by hydrochloric acid. The author has followed the course of the action by quantitative determinations.

* The author seems to be unaware that Dr. W. J. Russell has shown conclusively that hydrogen precipitates metallic silver from a solution of silver nitrate (this Journal, 1874, 3).—Editors.

The action of nearly pure hydrogen phosphide on concentrated silver nitrate solution results in an explosion; if the gas be considerably diluted with hydrogen, the first phase of the reaction is expressed by the equation

$$PH_3 + 6AgNO_3 = 2(Ag_3P,3AgNO_3) + 3HNO_3.$$

The yellow double compound formed is more stable than those containing arsenic or antimony, but blackens on adding water, leaving a mixture of silver and silver phosphide, which evolves hydrogen phosphide on treatment with zinc and hydrochloric acid. The yellow substance soon decomposes on exposure to the air, leaving metallic silver. Dilute solutions of silver nitrate yield at once the black mixture of silver and silver phosphide, and the solution is found to contain nitric, nitrous, phosphoric, and hypophosphorous acids. This reaction would be useless as the basis of a method for determining phosphorus similar to those afforded by the action of hydrogen arsenide and antimonide on silver nitrate solution. W. J. P.

Atomic Weight of Boron. By E. Rimbach (*Ber.*, **26**, 164—171).—The author has redetermined the atomic weight of boron from the amount of sodium contained in crystalline borax, the estimation of the sodium being made by titration with hydrochloric acid of known strength, using methyl-orange as indicator. The latter is not changed by boric acid, and only undergoes change when the whole of the sodium in the borax has been converted into the chloride.

The borax was prepared from pure boric acid by treating it with the theoretical quantity of pure sodium carbonate, recrystallising the product three times, and drying in the air until the loss of weight was almost inappreciable; the hydrochloric acid employed was carefully purified, and all titrations carried out in vessels made of glass which was only attacked very slightly by water. The mean result showed that the atomic weight of boron (O = 16, H = 1·0032) is 10·945, which agrees closely with the number recently obtained by Ramsay and Aston (Trans., 1893, 207), but differs by 0·1 from that found by Abrahall (Trans., 1892, 650). H. G. C.

Silver. By M. C. Lea (*Amer. J. Sci.* [3], **44**, 444—446).—Aqueous ammonia has a distinct solvent action on silver reduced from the nitrate by sodium hydroxide and lactose, or reduced from the chloride by cadmium and hydrochloric acid. If the solutions are evaporated to dryness on a water-bath, brown-black, non-explosive residues are left, which dissolve almost completely in acetic acid, leaving a small quantity of metallic silver which has probably been reduced by organic matter in the ammonia. The acetic acid solution contains a considerable quantity of silver, and it is evident that the silver dissolves in the form of oxide.

Aqueous ammonia has no solvent action on silver when air is completely excluded.

Almost any form of finely divided silver is distinctly soluble, contrary to the usual statement, in sulphuric acid diluted with four or five times its bulk of water, but with more dilute acid the different

forms of the metal behave very differently. The form most easily attacked is that obtained by reduction with an alkali hydroxide and lactose, and this is distinctly soluble in sulphuric acid diluted with 100 times its volume of water. Acid of this strength has no action at all on silver reduced from the chloride by cadmium.

Nitric acid of sp. gr. 1·40, diluted with water to 10 volumes and allowed to remain in contact with finely divided silver for an hour, dissolves only a minute trace of the metal. Hydrochloric acid of sp. gr. 1·20 is entirely without action on metallic silver, and this is true also of acetic acid.

Normal silver, even when in a fine state of division, is not attacked in the slightest degree by perfectly neutral copper nitrate solution obtained by the action of copper sulphate on barium nitrate, even after 15 hours contact. On the other hand, silver readily reduces cupric chloride with formation of the purple photochloride, and if the cupric salt is present in slight excess, the change is so complete that the product is quite insoluble in nitric acid. Metallic mercury instantly reduces silver nitrate, but silver, on the other hand, reduces mercuric chloride.

A solution of ferric alum readily dissolves silver at the ordinary temperature, with production of a ferrous salt, and if the ferric compound is in excess, the whole of the silver is dissolved. When ferrous sulphate solution is mixed with successive quantities of silver oxide until a fresh quantity of the latter is no longer affected, the whole of the iron is precipitated, and a black product is obtained which is probably the compound $Ag_4O,2FeO,Fe_2O_3$, obtained by H. Rose in the same way.

When a solution of ammonium ferric alum is mixed with a large excess of finely divided silver in a well closed vessel and allowed to remain for several days, with frequent agitation, the liquid acquires a deep red colour, which may persist for several days, but then gradually disappears, the solution becoming greenish, although it still contains a considerable quantity of ferric salt. It follows that the reducing action of silver on ferric salts is limited and ceases before reduction is complete, even when the silver is present in large excess.

C. H. B.

Silver Chloride. By M. C. Lea (*Amer. J. Sci.* [3], **44**, 446—447).—Acworth has observed that when silver chloride is heated at 220° it becomes insensitive to light. The author considers that this result is due to complete expulsion of the moisture. Silver chloride, after being dried in hot air, always loses from 0·5 to 1·0 milligram per gram when melted. C. H. B.

Action of Dried Hydrogen Chloride on Iceland Spar. By R. E. Hughes and F. R. L. Wilson (*Phil. Mag.* [5], **34**, 117—120).—Hydrogen chloride was passed over copper turnings and through tubes containing pumice moistened with sulphuric acid, and finally pumice and phosphoric anhydride. The gas thus purified and dried was then passed over a weighed quantity of Iceland spar at 130° for about an hour, at the end of which time the spar was again weighed.

No practical increase in weight was noted. Moist hydrogen chloride occasioned an increase of 0·02 gram on 0·69 gram of Iceland spar.
J. W.

Constitution of Bleaching Powder as elucidated by its Dissociation. By J. MIJERS (*Rec. Trav. Chim.*, **11**, 76—83).—The author's results lead him to the view that bleaching powder is not identical with the compound obtained by Lunge by passing a current of hypochlorous anhydride over hydrated calcium chloride. He regards bleaching powder as a compound of calcium hydroxide with chlorine, $Ca(OH)_2Cl_2$; and to the active compound he ascribes the formula $CaOCl_2$. It is only possible to prepare bleaching powder free from uncombined calcium hydroxide at very low temperatures.
A. R. L.

Note.—The author does not allude to Dreyfus' experiments (Abstr., 1885, 19), who arrives at a different conclusion (compare, however, Lunge and Schoch, Abstr., 1887, 700). A. R. L.

Complete Elimination of Barium from Strontium Salts. By BARTHE and FALIÈRES (*Bull. Soc. Chim.* [3], **7**, 473—475).—A reply to the criticisms of Cannepin (*Union pharmaceutique*, 1892, 1), on the authors' process (Abstr., 1892, 1277). A. R. L.

Magnesium Nitride. By S. PASCHKOWEZKY (*J. pr. Chem.* [2], **47**, 89—94).—The author has carried out Merz's method for making magnesium nitride (Abstr., 1892, 409) on a somewhat larger scale. 20—25 grams of powdered magnesium was spread in a layer 0·9—1 m. long in a combustion tube of 11—12 mm. diameter, and heated in a current of well dried ammonia. The nitride thus produced contained 27·84 per cent. of nitrogen (theory = 28 per cent.). The orange surface-colour appears when the heating is strongest, but has no appreciable influence on the percentage of nitrogen. The nitride was also produced by the direct absorption of nitrogen by the hot magneesium. A. G. B.

Purification of Arsenical Zinc. By H. LESCŒUR (*Compt rend.*, **116**, 58—60).—Fusion of zinc with potassium nitrate removes sulphur and phosphorus, but does not remove arsenic and antimony, whilst fusion with ammonium chloride or magnesium chloride expels arsenic and antimony, but does not affect the sulphur and phosphorus. In order to obtain pure zinc for toxicological purposes, both modes of treatment must be applied, the metal being first fused with potassium nitrate, and afterwards with a chloride or *vice versâ*. Zinc chloride is preferable to either ammonium or magnesium chloride for this purpose. The double treatment removes arsenic, antimony, sulphur, and phosphorus, but does not, of course, remove metals such as copper, lead, or iron. C H. B.

Preparation of Acicular Basic Zinc Nitrate. By A. TERREIL (*Bull. Soc. Chim.* [3], **7**, 553—554).—A solution of zinc nitrate is boiled for an hour or two with an excess of metallic zinc, and then

evaporated at a gentle heat to a syrup, which solidifies on cooling. The mass is now extracted with cold water, which dissolves the normal nitrate, leaving the basic nitrate in the form of delicate needles of the composition $5ZnO,N_2O_5 + 5H_2O$.

These needles, when heated, lose first water and then nitric anhydride, leaving a pseudomorph of zinc oxide, which retains a slight yellow colour when quite cool. A certain quantity of ammonium nitrate is formed and nitric oxide is evolved when the basic nitrate is treated with nitric acid. A. R. L.

Dehydration of Copper Hydroxide and certain of its Basic Compounds in the presence of Water. By W. Spring and M. Lucion (*Zeits. anorg. Chem.*, **2**, 195—220).—Copper sulphate was precipitated in the cold with alkali hydroxide, and the blue hydrated oxide, after washing, suspended in water. Equal quantities were then introduced into a flask containing either pure water or a solution of one of the salts mentioned below. It is found that the freshly-precipitated compound is only completely dehydrated in contact with pure water at 15° after 9 months, at 30° after 86 hours, at 45° after 38 hours, and the hydrated oxide cannot exist above 54°. The dehydration proceeds the more slowly the longer the time which has elapsed since its preparation. The freshly-precipitated blue compound has the composition $CuO + 2H_2O$, and this hydrate, after being for some hours in contact with water at 15°, is converted into the brown monohydrate $CuO + H_2O$, which is then further dehydrated more slowly. At temperatures of 30° and 45°, and in the presence of certain salts, the dehydration is expedited; it, however, proceeds more slowly after reaching the monohydrate stage. The salts employed were the following:—Sodium and potassium hydroxides, sodium and potassium chlorides, potassium bromide, potassium iodide, barium chloride, zinc chloride, sodium sulphate, magnesium sulphate, manganese sulphate, and potassium nitrate. The electrolytic dissociation of these salts appears to have some connection with their dehydrating powers, but the exact relation between the dehydrating powers and the osmotic pressures of the salts could not be traced from the data at hand, which were complicated in certain cases by the formation of intermediate basic salts. Thus, in the case of the haloïd salts, colloïdal compounds of the general formula $Cu_2X_2,CuO + 3H_2O$ result. This formation of cuprous compounds from cupric without the intervention of a reducing agent is thus explained:—When pure hydrated copper oxide is triturated with a solution of potassium bromide at 25°, after a while an evolution of oxygen takes place, and the filtrate is found to contain hydrogen peroxide. The following reactions occur. (1) $3\,Cu(OH)_2 + 2KBr = Cu_2Br_2,Cu(OH)_2,H_2O + K_2O_2,H_2O$. (2) $K_2O_2,H_2O = 2KOH + O$. When hydrated copper oxide is mixed with a solution of copper chloride, and the excess of the latter removed by dialysis, the compound $Cu_2Cl_2,CuO,3H_2O$ is directly synthesised. The author finally discusses the important geological bearing of these results.

A. R. L.

Molecular Weight of "Gadolinium Oxide." By A. E. NORDENSKIÖLD (*J. pr. Chem.* [2], **47**, 1—27; compare Abstr., 1887, 109).—By the term "gadolinium oxide," the author implies that group of earthy oxides which are precipitated from the solution of their sulphates by ammonia and by oxalic acid, but not by an excess of normal potassium sulphate. A new series of determinations of the equivalent of this group of oxides has been made, and a list of the values obtained for the oxide from 54 minerals is given. These only vary from 275·8 to 247·9, or ±5·4 per cent. from the mean, 262, notwithstanding the fact that the equivalents of the individual oxides contained in the "gadolinium oxide" vary between 136 and 394, if scandium be included, or between 227 and 394 if this be excluded. It is notable that in most cases where different minerals contain closely allied elements, a given mineral will contain only one of these elements, or at all events chiefly one with small quantities of another or others. For example, the determination of the equivalent of the earthy oxide in a calcium, barium, or strontium mineral will almost always approximate very closely to the equivalent of lime, baryta, or strontia. This is not so with the minerals containing the group of gadolinium oxides. All determinations of the equivalent in question made by previous observers which are, in the author's opinion, trustworthy agree with the limits given above. A list of these other determinations is given, and the author's methods are described.

A. G. B.

The Alloys of Iron and Tin. By W. P. HEADDEN (*Amer. J. Sci.*, **44**, 464—468).—From a study of the formation of the alloys of tin and iron, the author concludes that there is a series of iron stannides, of which he obtained the following members: $FeSn_2$, Fe_2Sn_3, Fe_3Sn_4, Fe_4Sn_5, Fe_5Sn_6, FeSn, Fe_3Sn, Fe_4Sn, and Fe_9Sn. Some of these have been described before; but the published descriptions assign to them properties some of which differ widely from those observed by the author.

B. H. B.

Roussin's Salt. By L. MARCHLEWSKI and J. SACHS (*Zeit. anorg. Chem.*, **2**, 175—181).—The author has confirmed the formula $Fe_4(NO)_7S_3K + H_2O$, assigned by Pavel (Abstr., 1883, 297) to Roussin's salt, by analysis, and by a determination of the molecular weight by Beckmann's boiling point method in ethereal solution. The compounds analysed by Roussin and by Rosenberg were impure, but on adding thallium sulphate to an aqueous solution of these preparations, a salt separates, which, when crystallised as rapidly as possible from alcohol in a vacuum, has the composition $Fe_4(NO)_7S_3Tl + H_2O$; it is very sparingly soluble in water, and decomposes on protracted heating with it.

A. R. L

Cobalt. By H. REMMLER (*Zeit. anorg. Chem.*, **2**, 221—234).—The material employed in this research was prepared from 1200 grams of cobalt chloride. The salt was dissolved in the smallest possible quantity of distilled water, and the filtered solution warmed with bromine water (1 litre), and potassium hydroxide added, until the mixture was distinctly alkaline; it was then warmed for two hours,

and the hydrated oxide washed by decantation 15 times, with about 6 litres of water, and finally thrown on to a filter, and the washing continued until the filtrate was free from chloride. The hydrated oxide was then treated with successive quantities of ammonia, which dissolves it slowly. In this way in the space of nine months, 25 fractions were obtained. The ammoniacal extracts were then purified, and finally converted into cobaltous oxide, and thence, by ignition of the latter in a current of dry carbonic anhydride, into cobaltic oxide. The fractions were found on qualitative examination to be free from iron, manganese, and nickel. Atomic weight determinations were made by weighing the amounts of cobalt obtained by igniting the oxide representing the various fractions in a current of hydrogen. The results lie between 59·53 and 58·3, differences far beyond the experimental error of the method, so that the author comes to the same conclusion as Krüss and Schmidt, namely, that cobalt purified by the ordinary method is not a homogeneous substance. A. R. L.

Determination of the Atomic Weight of Nickel. By G. Krüss and F. W. Schmidt (*Zeit. anorg. Chem.*, **2**, 235—254).—Continuing their experiments (Abstr., 1889, 349 and 1114), the authors have not succeeded in isolating a new element in the pure state from nickel; they find, however, that the metal prepared by carefully reducing the oxide in a current of hydrogen is not homogeneous, even when it gives the usually accepted atomic weight 58·6. The fact cited by Winkler (Abstr., 1889, 760) that nickel which has not been fused imparts slight alkalinity to water is discussed, and the following experiment is described. A quantity of the nickel used for the atomic weight determination by Zimmermann (Abstr., 1886, 596) was warmed with water on the water-bath for almost a year; from the resulting greenish-coloured solution, a small quantity of a substance was isolated after conversion into sulphate. Two solutions containing known quantities of the latter were precipitated with potassium hydroxide, and the oxide weighed; from these data, the substance appears to have been derived from an element having an equivalent between 35 and 45. The process cannot, however, be employed for the quantitative separation of the impurity, and numerous other fruitless attempts were made to obtain pure nickel. Ultimately the following experiments were conducted. Nickel oxide, rendered free from all known impurities with the exception of cobalt, was reduced in a current of pure dry hydrogen, at as low a temperature as possible, and subsequently treated with carbonic oxide. The gases which were evolved were passed through a series of flasks containing aqua regia, whereby the nickel carbonyl was decomposed, and the metal retained as chloride. The residue which had not volatilised was then treated successively with hydrogen and carbonic oxide as before, and this was repeated 10 times, so that 10 fractions were obtained, which were converted into metal. Atomic weight determinations were then made with each of the fractions, as follows. A portion of the metal was converted into the oxide, and the weight of metal obtained on reducing the latter with hydrogen ascertained. The metal was also quantitatively converted

into oxide, and the oxide again reduced. The results differed among themselves to an extent beyond the experimental error of the methods. The authors conclude, however, that the atomic weight of nickel is at most 58·1, and it would seem that a foreign metal, whose atomic weight is greater than 58·5, is present in nickel, and that when the oxide is reduced in a current of hydrogen, this element is in part volatilised. The residual metal left from the tenth fraction was freed from cobalt and converted into five fractions as oxide. The latter gave atomic weights varying between 59·17 and 64. A. R. L.

Action of Hydrogen Fluoride on certain Fluorides and Oxyfluorides. By A. Piccini (*Zeit. anorg. Chem.*, **2**, 21—24; compare this vol., ii, 124).—The author has now prepared *potassium fluoroxypertungstate*, $WO_3F_2,2KF + H_2O$; *fluoroxyperniobate*,

$$NbO_2F_3,2KF + H_2O;$$

and *fluoroxypertantalate*, $TaO_2F_3,2KF + H_2O$. These compounds were obtained in the same way as the potassium fluoroxypermolybdate, $MoO_3F_2,2KF + H_2O$, previously described, and resemble that substance closely in their properties. The substances from which they were prepared, $WO_2F_2,2KF + H_2O$, $NbOF_3,2KF + H_2O$, and $TaF_5,2KF$ respectively, were themselves obtained from potassium tungstate, niobic acid, and tantalic acid respectively, by treatment with hydrofluoric acid. C. F. B.

An Acid Potassium Platonitrite. By M. Vèzes (*Compt. rend.*, **116**, 99—102).—When a solution of potassium platonitrite containing any free acid, or an acid solution of a halogen derivative of the platonitrite, is concentrated, a new compound is formed and separated as a red crust made up of very slender needles.

In order to obtain this product in considerable quantity, a warm, concentrated solution of the platonitrite is mixed with an exactly equivalent quantity of sulphuric acid, so that the composition of the mixture is $K_2Pt(NO_2)_4 + H_2SO_4$. The green solution, when strongly concentrated by heat, gives off nitrogen oxides, and on cooling deposits slender, red needles which can be recrystallised from hot water. They have the composition $K_2H_4Pt_3O(NO_2)_6 + 3H_2O$, lose their water of crystallisation in dry air or at 100°, and decompose with effervescence when strongly heated.

Titration of a solution of the salt with potassium hydroxide, using litmus as an indicator, shows that neutrality is reached when 1 mol. of potassium hydroxide has been added to 1 mol. of the salt, and hence the formula of the latter would be $Pt_3O(NO_2)_6K_2H$. If, however, phenolphthaleïn is used as the indicator, 4 mols. of the alkali are required to produce neutrality, and hence the formula of the salt would be $K_2H_4Pt_3O(NO_2)_6$, as already stated. Further experiments are in progress with a view to decide this question. C. H. B.

Rhodium Salts. By T. Wilm (*Zeit. anorg. Chem.*, **2**, 51—63).—In addition to the two double salts (1) $Rh_2Cl_6,6NH_4Cl + 3H_2O$, and (2) $Rh_2Cl_6,4HCl + 2H_2O$, the author previously (Abstr., 1884, 660;

Ber., **16**, 3033) described a third, (3) $Rh_2Cl_4,8NH_4Cl + 7H_2O$. He now confirms Leidié's conclusion (*Bull. Soc. Chim.* [2], **50**, 664), that this salt is really a chloronitrate, (4) $Rh_2Cl_4,6NH_4Cl,2NH_4NO_3$. It is formed when much aqua regia is present in the solution. Water decomposes it, with formation of the salt (2); but, on the other hand, it is itself formed from this salt by the addition of ammonium nitrate. Curiously enough red, hexagonal plates, precisely similar to those of (4), are often obtained when the salts (1) and (2) crystallise out from solutions which do not contain any nitric acid, but these crystals are unstable, and rapidly change, usually into prismatic crystals of (2).

C. F. B.

Action of Chlorine and Carbonic Oxide on Iridium. By U. Antony (*Gazzetta*, **22**, ii, 547—548).—The author has previously stated (Abstr., 1892, 1285) that iridium gives no trace of a volatile compound at 240° in a current of chlorine and carbonic oxide, whilst Mylius and Foerster (Abstr., 1892, 789) found that iridium is slightly volatile in such a gaseous mixture. Foerster (*Ber.*, **25**, Ref. 441) attributes this seeming contradiction to a difference in the conditions under which the two sets of experiments were conducted; the author, however, cannot recognise this difference, and, after repeating his experiments, confirms his previous results.

W. J. P.

Mineralogical Chemistry.

Artificial Production of Mineral Sulphides. By H. N. Warren (*Chem. News*, **66**, 287).—By heating with potassium thiocyanate, litharge is converted into galena, even at a low red heat; whilst at the heat of fusion, the product has the same cleavage and almost the same sp. gr. as the native mineral. With the same reagent, iron oxide yields brilliant pyrites at a red heat, and Fe_2S_3 at a higher temperature; manganic oxide yields pyrolusite at bright redness; stannic and antimonic oxides yield the golden-yellow sulphides at low temperatures, and the ordinary sulphides at higher temperatures; and zinc oxide also yields a sulphide which exhibits phosphorescence in a marked degree.

D. A. L.

Aguilarite. By F. A. Genth (*Amer. J. Sci.*, **44**, 381—383).—The author gives analyses of several varieties of aguilarite: (*a*) irregular, flat particles in calcite; (*b*) small, capillary, needle- and wire-shaped individuals with small crystals, apparently hexagonal; (*c*) similar crystals, seen under the microscope to be made up of different minerals, the outer portion (1) being brittle, and the inner (2) malleable; and (*d*) solid dodecahedral crystals. The analytical results were as follows:—

	Ag.	S.	Se.	Cu.	Fe.	Sb.	As.	Total.
a.	79·41	5·93	13·96	0·50	—	—	—	99·80
b.	80·27	6·75	12·73	0·07	0·26	0·41	—	100·49
*c*1.	67·58	3·51	14·76	6·83	0·42	6·83	—	99·93
*c*2.	84·05	3·82	8·76	1·83	—	1·24	0·28	99·98
d.	84·40	11·36	3·75	0·49	—	—	—	100·00

B. H. B.

Metacinnabarite. By F. A. Genth (*Amer. J. Sci.*, **44**, 383).—A specimen of metacinnabarite from San Joaquin, Orange Co., California, occurring in irregular particles in barytes, gave, on analysis, the following results:—

Hg.	S.	Cl.	Total.
85·89	13·69	0·32	99·90

It is remarkable that all the fragments that were examined showed the presence of chlorine. B. H. B.

Danalite. By F. A. Genth (*Amer. J. Sci.*, **44**, 385—386).—The occurrence of the rare mineral danalite, at Cheyenne Cañon, El Paso Co., Colorado, is described by the author. The fragment examined is part of a modified tetrahedron, with a sp. gr. of 3·626 to 3·661. Analysis yielded the following results:—

SiO_2.	BeO.	CuO.	ZnO.	FeO.	MnO.	S.	Ignition.
30·26	12·70	0·30	46·20	6·81	1·22	5·49	0·21

These results closely agree with the formula $(Be,Zn,Fe,Mn)_7Si_3O_{12}S$. In the same paper, the author gives analyses of rutile, of quartz resulting from the alteration of flesh-coloured orthoclase, and of yttrium-calcium fluoride from the same locality. He also gives analyses of löllingite from North Carolina, of altered zircon or cyrtolite from Mt. Antero, Colorado, of lepidolite from Japan, and of fuchsite from Habersham Co., Georgia. B. H. B.

Phosphoric acid in Beryl. By F. C. Robinson (*Chem. News*, **66**, 297).—A sample of beryl, in colour grey to white with a mere trace of green, with a hardness of 7, and sp. gr. 2·627, lost, on drying at 100°, 0·33 per cent., and, on analysis, gave the following numbers:—

SiO_2.	Al_2O_3.	BeO.	P_2O_5.	(Na_2O,K_2O,Li_2O,Cs_2O).	Loss on ignition.	Total.
64·70	17·76	12·18	2·76	1·10	1·53	100·03

Regarding the phosphoric acid and alkalis as replacing a part of the beryllium, the molecular ratios for water, alumina, beryllium oxide, and silica are respectively 1, 2, 3, 12, showing that the mineral is a beryl. Other specimens of beryl have since been tested, and phosphoric acid has been detected in nearly every case, but in none of them in such a large proportion as 2·76 per cent. D. A. L.

Mt. Joy Meteorite. By E. E. Howell (*Amer. J. Sci.*, **44**, 415—416).—This meteorite, the third largest in the United States, was found in November, 1887, in the township of Mt. Joy, Pennsylvania. The three largest dimensions of the meteorite are 11, 24, and 33½ inches, and its weight is 847 lbs. Analysis yielded the following results:—

Fe.	Ni.	Co.	Cu.	P.	S.	Total.
93·80	4·81	0·51	0·005	0·19	0·01	99·325

The results of an examination of the magnetic properties shows that the meteorite as a whole acts as a mass of soft iron gaining polarity under the inductive action of the earth. B. H. B.

Meteorite of Grossliebenthal. By P. Melikoff and C. Schwalbe (*Ber.*, **25**, 234—241).—The meteorite fell in November, 1881, at Grossliebenthal, near Odessa. It weighed over 8 kilos., and is covered with a black crust 1—1·5 mm. thick. The bulk of the meteorite is ash-grey and finely granular, and contains angular pieces of metal which are attracted by a magnet, and also pieces of iron sulphide and iron chromite. Its sp. gr. = 3·584 at 20°. An analysis gave the following results:—

H_2O.	SiO_2.	MgO.	CuO.	FeO.	MnO.	Al_2O_3.	Na_2O.	K_2O.	Fe_7S_8.
0·10	39·57	22·97	2·28	13·44	0·53	2·45	1·30	0·45	6·73

$Fe_{11}Ni_2$.	$FeCr_2O_4$.	P.	P_2O_5.	Cl.	Total.
8·16	1·30	0·02	0·21	0·04	99·55

It also contained traces of chromium and metals precipitated by hydrogen sulphide.

The silicates insoluble in hydrochloric acid had a sp. gr. = 3·179. The total silicates amount to 82·99 per cent., and consist of olivine 43·30 per cent., bronzite 26·87 per cent., and albite 12·82 per cent. E. C. R.

Water and Sea-bottom Deposits of the Eastern Mediterranean. By K. Natterer (*Monatsh.*, **13**, 873—896, 897—915).—In these papers, the author gives an account of a large number of analyses of sea water and sea-bottom deposits made during the voyages of the ship "Pola" in 1890 and 1891. The area investigated formed a quadrilateral, which lay between the islands of Corfu and Santorin on the European coast, and Ben-Ghâzi and Alexandria on the African coast. The tabulated results show that the substances dissolved in sea water were present in almost constant proportions in all the samples examined; but a noteworthy reduction in the quantity of bromine was observed in the neighbourhood of the African coast to the west of Alexandria. This reduction is, perhaps, to be attributed to the action of living plants, which store up bromine in the same way as they do iodine.

The author further gives the results of an analysis of the spring water used for supplying the Arsenal in the island of Crete. G. T. M.

Physiological Chemistry.

Influence of Chloroform on Peptic Digestion. By A. BERTELS (*Virchow's Archiv*, **130**, 497—511).—Chloroform exercises a destructive influence on Finzelberg's pepsin in artificial digestive mixtures, if it is added to saturation; air passed through the mixture has the same effect. But if fresh mucous membrane from the pig's stomach is used instead, neither chloroform nor air has the effect.

W. D. H.

Behaviour of Sterilised Milk towards Digestive Fluids. By ELLENBERGER and HOFMEISTER (*Expt. Stat. Record*, **4**, 311; from *Molk. Zeit.*, 1892, No. 6).—When sterilised milk is consumed, there is no formation of cheese in the stomach, as is the case with fresh milk, and the action of the acids of the stomach is very incomplete. The sterilised milk remains in a more or less liquid state, and may pass too soon into, and even through, the intestines. Further experiments on the relative digestibility of raw and sterilised milk are wanted.

N. H. M.

Accumulation of Strontium Bromide in the Organism. By C. FÉRÉ and L. HERBERT (*Compt. rend. Soc. Biol.*, 1892, 45).—Three experiments were made on rabbits; 1 gram of strontium bromide was given by the œsophagus daily. Death occurs more rapidly than with potassium bromide. The following numbers represent the daily amount given per kilo. of body weight, and that recovered in the tissues after death:—

	Dose.	Recovered.
1.....	4 doses of 0·59	1·715 per kilo.
2.....	9 doses of 0·76	2·121 „
3.....	10 doses of 0·438	1·57 „

Accumulation thus occurs much in the same proportion as with potassium bromide.

W. D. H.

Accumulation of Potassium Bromide in the Organism. By C. FÉRÉ and L. HERBERT (*Compt. rend. Soc. Biol.*, 1892, 130—132).—In two epileptics, who had for lengthy periods been treated with potassium bromide, *post-mortem* analysis indicated a predominance of accumulation of the drug in the cerebellum as compared with other parts of the nervous centres, but the greatest accumulation was in the nerves and liver.

W. D. H.

Localisation of Mercury in the Animal Organism. By ULLMANN (*Chem. Centr.*, 1892, ii. 941; from *Pharm. Post*, **25**, 1099—1101).—The author employed Ludwig's method (this vol., ii, 243) for the detection of the mercury. The distribution of the mercury in the organism always follows the same laws whatever the dose or the form of administration. The largest amount of mercury is found in the kidneys, liver, and spleen, in the order given. As regards the

digestive tract, the stomach contains very small but weighable quantities, whilst more is found in the small intestine, and still more in the large intestine. Small weighable quantities are found in the heart and skeletal muscles and in individual cases, also in the lungs. The brain, salivary glands, abdominal gland, thyroid gland, bile, and bone substance contain unweighable traces, or, with small doses, not even a trace of mercury. A. J. G.

Keratohyalin. By P. Ernst (*Virchow's Archiv*, **130**, 279—296).—This paper is chiefly histological. It discusses the question of what keratohyalin is. This name was given by Waldeyer to the substance in the cells of the *stratum granulosum* of the epidermis. It stains very differently to eleidin, the substance in the *stratum lucidum*. Eleidin, however, is not fat as some have considered.

The proposition is advanced that keratohyalin is nucleïn, or, at least, a derivative of nucleïn. It is certainly not keratin, nor is it hyalin. W. D. H.

Hyalin and Colloïd. By P. Ernst (*Virchow's Archiv*, **130**, 377—417).—By the use of aniline and other dyes, microchemical differences can be shown to exist between the various substances included under the names hyalin and colloïd; and these are again different from mucin.

There appear to be two varieties of hyalin in hyaline degeneration (for instance, of muscle); one is derived from epithelial cells, being a degeneration or secretion product. In this category is included the colloïd of the thyroid, many colloïd renal casts, and the ovarian colloïd. The other variety arises from the connective tissues and the vascular apparatus; it is stained reddish-purple by acid solutions of magenta. To this category belong the hyaline degeneration of the interfollicular tissue of the thyroid, the hyaline residue of the *theka follicularis* of the ovary, and the more or less hyaline glomeruli of the kidneys and the hyaline network of tumours. W. D. H.

Alkalinity of the Blood during Muscular Work. By W. Cohnstein (*Virchow's Archiv*, **130**, 332—360).—The following are the conclusions drawn from the experiments described:—

1. The alkalinity of the blood, both in carnivora and herbivora, decreases during muscular work.

2. The decrease goes on in herbivora *pari passu* with the work. In carnivora a minimum is soon reached, a regulating mechanism being apparently called into play to inhibit further lowering of the alkalinity.

3. The diet has considerable influence on the alkalinity of the blood in resting and working animals. By lessening the proteïd intake, carnivora are made similar to herbivora, in that the alkalinity of their blood undergoes more striking changes. W. D. H.

Glycogenic Function in Winter Frogs. By Dewevre (*Compt. rend. Soc. Biol.*, 1892, 19—21).—Contradictory statements as to the liver glycogen in frogs may be reconciled by considering the time of

year at which the observation is made. At the end of the hibernal period, there is no glycogen in the liver and no sugar in the blood. At the beginning, there is glycogen in the liver and sugar in the blood. Ablation of the liver in such animals does not cause the complete disappearance of sugar in the blood.

The rate at which the glycogen disappears from the liver varies in different frogs. It may be found absent after two weeks; in other cases 16 weeks may be necessary. The glycogen in the muscle increases as that in the liver goes, but in time the muscular glycogen is also used up.

All animals are not like the frog in these particulars: the marmot, for instance, becomes diabetic during hibernation. W. D. H.

Secretion of Hydrochloric acid in Nervous Dyspepsia. By R. Geigel and L. Abend (*Virchow's Archiv*, **130**, 1—28).—87 cases of nervous dyspepsia were examined: nothing characteristic in the gastric juice was found. On the average, however, the gastric juice was rather concentrated, as far as the acid was concerned. The absolute quantity of acid secreted was normal in 38, below the normal in 38, and above the normal in 11 analyses. W. D. H.

Lymph Secretion. By E. H. Starling (*J. Physiol.*, **14**, 131—153).—When "peptone" (that is, proteose *plus* peptone) is injected into the circulation of a living animal, it disappears gradually, and may still be found in the plasma one to two hours after the injection. The method used was to add to the blood or plasma an equal volume of trichloracetic acid (10 per cent. solution). This reagent does not precipitate proteose or peptone, but completely precipitates the normal proteïds of the blood.

The disappearance from the blood is caused in the first place by a transfer of "peptone" to the lymph, so that shortly after the injection the lymph contains more "peptone" than the blood plasma itself. This transference is effected by the selective activity of the cells of the vessel wall, and it is probable that a preponderating part is played by the endothelial cells of renal capillaries.

There is no connection between the loss of coagulability induced by the intra-vascular injection of "peptone" and the amount of peptone present in the plasma at any given time after injection.

W. D. H.

Transmission of Alcohol to Milk. By F. Klingemann (*Exper. Stat. Record*, **4**, 311; from *Molk. Zeit.*, 1892, No. 5).—Doses of alcohol (25 to 200 c.c.) strongly diluted were given to goats at night, and the milk of the following day examined. With 100 c.c. of alcohol, the next morning's milk contained 0·15 to 0·3 per cent. of alcohol, but the night's milk was free from alcohol. With 200 c.c. of alcohol, the yield of milk was reduced to about one-third and contained, in the morning 0·35 and in the evening 0·1 c.c. (? per cent.) of alcohol. No alcohol was found in human milk after the consumption of small quantities of alcohol, but with increased consumption small amounts were found. N. H. M.

Milk of different Breeds of Cows. By P. Collier (*Exper. Stat. Record*, **4**, 263—267; from *New York State Stat. Rep.*, 1891, 139—162).—The observations recorded were made with 15 cows, and extended over one (the first) period of lactation in each case. As regards composition, the constituent which showed least variation was the ash, the highest percentage being 0·760 (Devon), and the lowest 0·698 (Ayrshire and American Holderness). Fat is the most variable —from 3·46 (Holstein-Friesian) to 5·61 (Jersey) per cent. Caseïn varied from 3·39 (Holstein and Holderness) to 3·91 (Jersey); sugar from 4·84 (Holstein) to 5·33 (Ayrshire).

The microscopic examination of the milk of the 15 cows of the six breeds included the actual counting and measurement of 44,836 globules. The results showed that with the advance of the period of lactation, the relative number of the smaller globules increases with considerable regularity. A table is given showing the percentage of the fat in different sized globules; the results are important as bearing on the behaviour of the milks in butter and cheese making.

N. H. M.

The Acids of Ox Gall. By Lassar-Cohn (*Ber.*, **26**, 146—151).—It has been previously shown (Abstr., 1892, 1114) that myristic, palmitic, stearic, and oleïc acids occur in ox gall, and can be separated in the form of their barium salts from a solution prepared in a suitable manner; when these barium salts are converted into sodium salts, the solution of the latter again treated with barium chloride, and the filtrate fractionally precipitated with hydrochloric acid, a brownish resin is obtained. This resin, on recrystallisation from glacial acetic acid, yields a colourless, crystalline acid, which has the composition $C_{24}H_{40}O_4$, and is identical with Latschinoff's choleïc acid, and with Mylius' deoxycholic acid; on oxidation with chromic acid, the crystalline acid is converted into dehydrocholeïc acid, $C_{24}H_{38}O_4$, identical with the compound described by Latschinoff. The quantity of choleïc acid obtained by the author amounted to only 0·085 per cent. of the bile employed, whereas Latschinoff, who used bile from St. Petersburg, found about 1·6 per cent.; this, therefore, is the second case in which a difference of composition in samples of bile of different origin has been established, Emich having already drawn attention to the variation in the quantity of glycocholic acid.

The mother liquors from the choleïc acid, obtained in the manner described above, contain cholic acid, the presence of which is due to imperfect washing of the precipitate of barium salts, and resinous acids.

For the estimation of cholic acid in bile the following process may be adopted:—The bile, 20 c.c., is mixed with sodium hydroxide, 2 grams, the solution boiled for 24 hours, and, after having been treated with carbonic anhydride, evaporated to dryness on the water-bath; the residue is extracted with boiling 96 per cent. alcohol, until free from the salts of organic acids which are only sparingly soluble in water, and the extract, after having been diluted with 4 vols. of water, is precipitated with a dilute solution of barium chloride, 0·5 gram. The filtrate is then acidified with hydrochloric acid, and the cholic acid extracted by shaking with ether, into which it readily

passes, because of the alcohol present; the alcoholic, ethereal solution is evaporated, and the residual cholic acid dried until constant.

A sample of fresh bile analysed in this way on November 20 was found to contain 4·86 per cent. of cholic acid; two other samples, examined a few days later, contained 4·68 and 4·69 per cent. respectively.

The percentage of the various acids present in bile which has been boiled with soda is as follows:—

Cholic acid....	4·790	Stearic acid	0·146
Choleïc acid...	0·085	Palmitic acid ...	
Myristic acid..	0·004	Oleïc acid	
Resinous acids	0·120	Loss	0·050

F. S. K.

Carbonated Albuminuria. By J. Gaube (*Compt. rend. Soc. Biol.*, 1892, 399—402).—The author has previously stated that the albumin in urine is combined with calcium as an albuminophosphate. He now introduces the term carbonated albuminuria, to indicate the excretion by the kidneys of small quantities of albumin combined with alkali carbonates. W. D. H.

Chemical Stimulation of Nerves. By E. W. Groves (*J. Physiol.*, **14**, 221—232).—The central portions of motor nerves (for instance, sciatic of frog) are much less irritable than the peripheral to chemical stimuli, though they are sooner killed by their action.

The irregularity, both in manner and extent, of the muscular response to a chemical stimulus stands in marked contrast to the exceedingly regular response to electrical stimuli.

Afferent nerves (for instance, vagus of rabbit) are almost unaffected by chemical stimuli. W. D. H.

Action of Inorganic Salts on the Heart. By W. H. Howell, Miss E. Cooke, and R. G. Eaton (*J. Physiol.*, **14**, 198—220.—Paraglobulin was prepared by the magnesium sulphate and carbonic acid methods; it was dissolved, and the solution used as an artificial circulation through the frog's heart. The heart, however, could not be made to beat well. Serum, with all its constituents untouched, is an excellent circulating fluid. There is, however, no loss in its proteïd contents after it has been passed through the heart. Serum decalcified by admixture with sodium oxalate, is also inefficacious in keeping the heart beating.

Ringer's fluid is a mixture containing no proteïds, but simply inorganic salts, approximately the same in amount and proportion as in blood. It keeps the heart going well; in one experiment here recorded for 30 hours. The heart had been thoroughly washed out with normal salt solution before the experiment, so there could have been little possibility of any blood being retained by the heart. An aqueous extract of serum (which had previously been dried and heated to coagulate proteïd matter) acts even better than Ringer's fluid, and the inorganic salts of milk, similarly obtained, act in the same way.

The saline matter in saliva, and saliva itself, will not maintain the heart's activity, but the salts obtained from the gastric secretion will do so. Kronecker and his pupils (Abstr., 1889, 632) have stated that serum albumin is the only substance that will maintain the heart's activity. They find that peptone will not do so, until it has been placed in contact with the gastric mucous membrane; the action of the epithelial cells is stated to be to regenerate albumin from the peptone. There is no chemical proof of this, but the fact that the mixture now keeps a heart beating is regarded as sufficient proof of the regeneration of albumin. The fallacy in reasoning here is obvious. These experiments, moreover, show that it is probably the admixture with the inorganic salts which gave the "peptone" power to keep a heart going. Some recent experiments with gum arabic (Heffter, *Arch. exper. Path. Pharm.*, **29**, 41) are to be explained also on the presence of calcium and potassium salts mixed with the arabin.

The most probable explanation of the way that inorganic salts act, is that they serve as chemical stimuli of the heart muscle.

W. D. H.

Physiological Action of Iodine Compounds. By L. Lapicque (*Compt. rend. Soc. Biol.*, 1892, 108—119).—Various iodine compounds doubtless owe their activity to the iodine they contain. The proof of free iodine in the body, after their administration, has never been given. In the present experiments, various compounds of iodine were injected into the vessels, and the time of onset and intensity of the symptoms noted. It was found that the toxic action of the injected material varies as one would expect from chemical considerations, based on the hypothesis that a decomposition of the compound occurs in the organism. The least stable compounds produce their effects most readily.

W D. H.

Action of Strontium Iodide on the Circulation. By L. Lapicque and A. Malbec (*Compt. rend. Soc. Biol.*, 1892, 499—500).—The first effect noticed is a slowing of the heart and a rise of blood pressure, followed by the opposite, and is thus very similar to that observed with potassium iodide. The primary effect is due to the strontium, not the iodine.

W. D. H.

Action of Iodides. By L. Lapicque (*Compt. rend. Soc. Biol.*, 1892, 536—540).—The main effect of the iodides is a lowering of arterial tension and acceleration of the heart. In producing this effect, iodides of calcium and potassium act with the smallest dose, then follow in order those of strontium and sodium.

The action appears to be independent of the medullary centres.

W. D. H.

Physiolcgical Action of Chloralcse. By Hanriot and C. Richet (*Compt. rend.*, **116**, 63—65).—See this vol. i, 247.

Physiological Action of Atropine and Pilocarpine. By J. P. Morat and M. Doyon (*Compt. rend. Soc. Biol.*, 1892, 707—710).—These two drugs act in an inverse way on the respiratory movements;

atropine accelerates, and pilocarpine slows them. They antagonise one another when administered successively. W. D. H.

Physiological Action of Cinchonamine Sulphate. By ARNAUD and CHARRIN (*Compt. rend. Soc. Biol.*, 1892, 671—672).—Cinchonamine, $C_{19}H_{24}N_2O$, obtained from the *Remijia Purdieana*, is poisonous; its sulphate provoking tonic convulsions. Like quinine, it is a febrifuge. W. D. H.

Physiological Action of Cupreïne and its Derivatives. By E. GRIMAUX and J. V. LABORDE (*Compt. rend. Soc. Biol.*, 1892, 608—613).—The physiological effects of these substances present great resemblances, differing in the degree of activity according to an ascending scale from cupreïne to quinopropyline. Quinine in the normal state is not antithermic, whilst these substances are. Not only is there lowering of temperature, but also stupefying and analgesic effects. W. D. H.

Toxic Action of Expired Air. By J. HALDANE and J. L. SMITH (*Journ. Pathol. and Bacteriol.*, **1**, 318—321).—Further experiments performed on Merkel's plan (*Arch. Hygiene*, **15**, 1) lend no support to Brown Séquard's hypothesis (supported by Merkel) that expired air contains a special organic poison. The results obtained confirm those previously published by the authors (Abstr., 1892, 1502). W. D. H.

Antiseptic Treatment of Wounds. By E. P. NILES (*Exper. Stat. Record*, **4**, 360; from *Virg. Stat. Bul.*, No. 18, 1892).—Lysol (2 per cent.) prevented the growth of micro-organisms and decreased the amount of suppuration when used for washing a wound on a horse. Creolin (1 per cent.) retarded the growth of pus-producing organisms, but did not destroy them in 15 minutes. Dermatole, iodole, aristole, zinc oxide, and mercuric chloride were found to be unsuitable. Mercuric chloride (1 : 1000) retarded the growth of organisms, but was not strong enough to be of use, whilst stronger solutions are injurious to the tissues. N. H. M.

Chemistry of Vegetable Physiology and Agriculture.

Bacteria of the Stomach. By A. L. GILLESPIE (*Journ. Pathol. and Bacteriol.*, **1**, 279—302).—Many organisms grow in the stomach even when its contents are acid. When organic acids are present, bacteria can be grown which produce the same acids in suitable media. Proteïd hydrochlorides have very little inhibitory power on organisms as compared with free hydrochloric acid. Excess of bacterial growth is deleterious to gastric and pancreatic digestion; the presence of bacteria fulfils a useful purpose in the intestine, the acids they produce controlling putrefaction. The formation of leucine and tyrosine does not seem to be aided by the presence of bacteria. W. D. H.

Liberation of Nitrogen during Putrefaction. By H. B. GIBSON (*Amer. Chem. J.*, 12—18).—Lean beef or blood serum covered with water was allowed to putrefy in a confined atmosphere, which was renewed from time to time by admitting purified air. The nitrogen was determined in a sample of the material at the beginning of the operations, water and either emulsion of putrid meat or soil infusion was then added to a known amount of material, and putrefaction allowed to proceed at the ordinary temperature for periods varying from 63 to 168 days. The volatile nitrogenous products of putrefaction, such as ammonia, indole, and skatole, were removed from the discarded air by sulphuric acid. At the end of the operations, the nitrogen was estimated in the whole of the putrefied material by the Kjeldahl process, and the loss, due allowance having been made for the volatile nitrogenous substances, calculated as nitrogen liberated during the experiment.

With putrid meat emulsion, the loss was small, ranging between 1 and 4·4 per cent., but with soil infusion it rose to 9·6—15 per cent. Nitrates and nitrites were not present at any stage of the operations, and hence, when putrefaction is started by means of soil infusion, there seems to be extensive direct conversion of organic into free nitrogen. JN. W.

Soluble Pentoses in Plants. By G. DE CHALMOT (*Amer. Chem. J.*, **15**, 21—38).—See this vol., i, 247.

Production of Albumin in Plants. Co-operation of Phosphoric acid. By A. MAYER (*Landw. Versuchs-Stat.*, **41**, 433—441).—Whilst it is maintained that phosphoric acid is necessary for albumin formation, manuring experiments show that nitrogenous matter applied alone induces much growth, and this can only be due to the organised nitrogen, inasmuch as the most important vegetative phenomena proceed from the highly nitrogenous protoplasm. In order to obtain some explanation of this, winter rye was grown in soil (very exhausted as regards phophates) and manured with nitrate and with kainite and superphosphate respectively. The rye receiving nitrate grew far more luxuriantly than the other. As was shown long ago by Arendt (with oats), the plants contained much more proteïds and ash in the early stages of growth than at subsequent periods. A more important point, as bearing more directly on the object of these experiments, was the fact that the percentage of pure proteïn in the crude proteïn was practically the same (about 70 per cent.) in the produce of both plots. Similar results were obtained with grass. The production of proteïds is thus very rapid, and intermediate products, as amides, do not exist for any length of time. As regards the amount of phosphoric acid in the plants of the two plots, there was no considerable difference. The soil, although much exhausted, contained too much phosphoric acid for the experiment. Accordingly, an infertile, siliceous, diluvial sand was next employed, manured on the one hand with sodium nitrate, gypsum, and kainite, and on the other with superphosphate and kainite. The plants (again rye) did not grow luxuriantly and the nitrate vessels did not pro-

duce much more than the others. The ears in Experiment 1 (nitrate) were larger than those in Experiment 3 (phosphate), but there were 3 more in No. 3. The results showed clearly that nitrate produces less, or at any rate not more, nitrogenous matter when phosphates are absolutely wanting. The absence of phosphates (and of nitrogen) gives rise to limited growth, and not to a growth of different composition, so that the forcing action of the nitrates hardly comes in.

The chief reason against heavy nitrogen manuring is not the waste of the most costly manure with insufficient representation of other manures, but the fear of injuring the crop, either through its becoming too bulky, in consequence of which the plants shade each other (hindering the production of carbohydrates), or by prolonging the development of the plants, thus delaying ripening.

The results of the above experiments do not dispose of the question of a connection between proteïds and a single ash constituent, phosphoric acid. N. H. M.

Composition and Nutritive Value of the Tubers of Stachys tuberifera. By F. Strohmer and A. Stift (*Bied. Centr.*, **21**, 820—822; from *Oest. ungar. Zeits. Zuckerind. u. Landw.*, 1891, 1—4).—The tubers contained 21·95 per cent. of dry matter. The percentage composition of the dry substance, freed from sand, was found to be as follows:—

Albumin.	Non-proteïds.	Crude fat.	Crude fibre.	Stachyose.	Pure ash.	Not determined.	K_2O.	P_2O_5.
5·34	14·33	0·73	3·33	63·50	5·48	7·20	2·62	1·00

The following numbers show the percentage amounts of nitrogen in various forms:—

Albumin.	Nucleïn.	Ammonia.	Amido-acid amides.	Amido-acids.	Not determined.
19·01	8·13	7·81	42·96	16·26	5·80

The nutritive value of the tubers resembles generally that of vegetables and potatoes, but they are more digestible and contain more nitrogenous nutritive matter (compare v. Planta, Abstr., 1890, 1183). N. H. M.

Composition of the Stems and Leaves of Tomatoes. Presence of Boron, Lithium, and Copper in the Plant. By N. Passerini (*Staz. Sper. Agrar.*, **20**, 471—476).—The author has already investigated the composition of the fruit of tomatoes (Abstr., 1891, 256). As regards the stems and leaves, the fresh stems contained 8·84—9·92 per cent. of dry matter, and 1·57—1·96 per cent. of crude ash; the fresh leaves contained 11·62—14·62 per cent. of dry matter, and 1·60—3·23 per cent. of crude ash. The dried stems and leaves contained respectively 1·8995 and 1·4374 per cent. of nitrogen. The percentage composition of the pure ash of (I) the stems and (II) the leaves was found to be as follows:—

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	Mn_3O_4.	P_2O_5.	SO_3.	SiO_2.	Cl.
I.	24·95	11·08	32·80	7·87	0·84	—	2·29	4·69	6·05	14·48
II.	1·95	1·37	38·14	9·00	0·14	0·05	1.36	12·79	33·84	1·83

A good crop (50,000 kilos. of fresh fruit per hectare), excluding the leaves, which are usually returned to the soil, would take from the soil: nitrogen, 113·7 kilos.; phosphoric anhydride, 50·7 kilos.; potash, 256·6 kilos.; lime, 58·4 kilos.; and magnesia, 23·8 kilos.

An aqueous extract of the ash of the stems, from which sodium and potassium had been separated, was examined spectroscopically, when the lithium line α was distinctly seen. Another portion of the extract was found to contain boron (Rose's method). The insoluble portion of the ash contained copper in quantity sufficient to be detected by means of ordinary reagents. In connection with this, it is mentioned that the plants analysed were grown in the open country, and that no copper preparation had been used for destroying injurious insects; in the analytical processes, the use of copper vessels was avoided. Barium and strontium could not be detected.

N. H. M.

Composition of Chick-Peas (Cicer arietinum). Presence of Boron, Lithium, and Copper in the Plant. By N. Passerini (*Staz. Sper. Agrar.*, **21**, 20—30).—The only analyses of chick-peas hitherto published seem to be those of Berthier (*Selmi's Enciclop. Chim.*, **4**, 449) and Ritter (*Bied. Centr.*, 1884, 529). The fresh substance of the stems, leaves, and the entire pods contains 27·54, 24·39, and 19·85 per cent. of dry matter (at 105°); in the dry matter of the various parts of the plant the following amounts of crude ash were found:—Stems, 10·44; leaves, 11·91; husks, 6·73; pods, 3·47. The dry matter of the seeds, amounting to 85·81 per cent. of the fresh substance, has the following percentage composition:—

Nitrogenous matter.	Fat.	Amides.	Sugar.	Cellulose.	Pure ash.	Nitrogen.
26·19	5·23	52·50	3·65	1·71	3·29	4·19

The seeds are thus particularly rich in nitrogenous matter, which represents more than a quarter of the whole. Seeds of beans and white kidney beans were found to contain 20·46 and 19·46 per cent. of nitrogenous matter respectively. The amount of amides in the seeds of chick-peas is also very remarkable.

The dry matter of (I) the stems, and (II) the leaves of chick-peas has the composition

	Nitrogenous matter.	Fat.	Cellulose.	Other carbohydrates.	Pure ash.	Nitrogen.
I.	6·35	1·83	34·96	49·05	7·81	1·02
II.	14·21	4·11	13·93	58·92	8·83	2·27

The percentage composition of the ash of (1) the seeds, (2) stems, and (3) leaves is given next.

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	Mn_3O_4.	P_2O_5.	SO_3.	SiO_2.	Cl.
1.	24·60	1·29	4·45	19·98	2·42	—	39·56	3·38	0·71	2·85
2.	48·38	0·45	23·55	4·38	2·14	0·03	5·29	5·79	6·21	3·78
3.	29·58	0·86	40·63	3·33	3·01	—	5·96	4·43	11·30	1·86

As in the case of other *Leguminosæ*, the percentage of potash in the

straw ash is very high; in fact, nearly half the total ash. The calcium is chiefly accumulated in the leaves, and the magnesium in the seeds. With regard to the more important constituents, a good crop of 80 kilos. of seeds and 2000 kilos. of straw per hectare would remove: nitrogen, 52·8 kilos.; phosphoric anhydride, 18·1 kilos.; potash, 74·6 kilos.; calcium, 34·3 kilos.; and magnesium, 11·5 kilos.

The examination for rare elements was carried out as already indicated (preceding abstract). The presence of boron was clearly shown; lithium was detected by means of the spectroscope, and copper was found in the pure ash of the stems to the extent of 0·082 per cent. This result, however, notwithstanding the care taken, is given with some reserve, as it seems rather high. N. H. M.

Composition of Iris germanica. Presence of Boron, Lithium, and Copper. By N. Passerini (*Staz. Sper. Agrar.*, **21**, 565—573). —The rhizomes, leaves, and flowers of *Iris germanica* contained in their natural state 42·19, 18·15, and 8·51 per cent. respectively of dry matter, and 1·34, 2·84, and 0·86 per cent. of crude ash. The following numbers show the percentage composition (I) of the dried rhizomes, and (II) of the dried leaves:—

	Nitrogen.	Nitrogenous matter.	Fat.	Cellulose.	Amides.	Glucose.	Not determined.	Pure ash.
I.	1·39	8·68	9·62	4·66	57·04	6·72	9·62	5·64
II.	0·77	4·83	2·24	23·56		59·50		9·87

The fatty matter when heated at 100° gives off a pungent, irritating vapour. The pure ash of (1) the rhizomes and (2) the leaves has the following percentage composition:—

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	Mn_3O_4.	P_2O_5.	SO_3.	SiO_2.	Cl.
1.	33·18	1·71	41·06	3·25	2·71	0·02	8·11	3·85	5·24	1·83
2.	37·18	1·05	42·74	2·92	0·49	0·03	7·28	3·40	1·47	1·93

Notwithstanding the high percentage of lime found in the ash, the plant is known to grow luxuriantly in soil containing only 0·85 per cent. of lime.

Boron and lithium were found in the ash of the leaves, and 0·022 per cent. of copper in the pure ash of the rhizomes. N. H. M.

Analyses of Oranges. By J. M. Pickell and J. J. Earle (*Exper. Stat. Rec.*, **4**, 346—348; from *Florida Stat. Bul.*, No. 17, 1892).— The average percentage composition of a large number of different kinds of oranges was found to be as follows:—

Dry matter.	Nitrogen.	Organic matter.
12·29	0·124	11·24

SiO_2.	SO_3.	P_2O_5.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Cl.
0·010	0·042	0·077	0·006	0·207	0·045	0·479	0·039	0·011

Different oranges of the same species differ sometimes very con-

siderably as regards ash constituents, the difference being due to variations in soil and climate. N. H. M.

Experiments with Wheat on the Substitution of Beryllium for Magnesium. By F. SESTINI (*Staz. Sper. Agrar.*, **20**, 256—258; compare *ibid.*, **15**, 290—298).—The experiments now described were similar to the earlier ones (*loc. cit.*), except that a white quartz sand was employed which had been previously boiled with hydrochloric acid. They were commenced the middle of February; there were two pots, each with ten seeds, but only three germinated, and at the end of May five more seeds were sown in each pot; four of them germinated. The plants were watered alternately with the nutritive solution containing beryllium and with distilled water. The growth was at first very slight, and the leaves very narrow. By the 15th June, four plants were 0·4 metre high, and on the 22nd one plant (0·52 metre high) began to form ear. Altogether six plants developed ears, one of which contained 8, another 5, and a third 1 grain, the rest being empty. The average weight of the grains was 0·026 gram.

The results of the experiments indicate that, whilst beryllium may take the place of magnesium in the growth of wheat, it is not a complete substitute for magnesium in the production of seed; under these circumstances, seed production becomes difficult, and the seed which is formed is little disposed to germinate. N. H. M.

Loss of Nitrogen in Manures. By A. MUNTZ and A. C. GIRARD (*Compt. rend.*, **116**, 108—111).—The authors have shown (this vol., ii, 181) that very serious loss of nitrogen takes place in the stables, &c., before the manure is put into heaps. Direct experiment shows that this loss is considerably reduced if an equal weight of peat is substituted for the ordinary straw litter. In a stable with 16 horses, the loss of nitrogen was 63·6 per cent. of that consumed when a straw litter was used, and only 48·3 with a peat litter. The loss is also less if dry earth rich in humic substances is used; in a sheepfold with 25 sheep, the loss was 50·2 per cent. with straw litter, and 25·7 per cent. with earth litter. The good effect of the earth depends on the quantity of humus that it contains. Direct experiments showed that the addition of small quantities of iron sulphate or calcium sulphate to the straw litter was practically without effect on the loss of nitrogen. A not inconsiderable proportion of the alkaline bases in the manure are non-volatile; the weight of sulphuric anhydride (SO_3), saturated by the non-volatile alkaline bases in 1 kilo. of manure, is as follows:—Horses, 1·352 gram; cows and oxen, 3·646 grams; sheep, 4·290 grams; pigs, 2·022 grams.

Taking into consideration the cost of material and subsequent treatment, it would seem that where peat is not readily accessible, the most useful plan would be to sprinkle earth, as rich in humus as possible, over the usual straw litter. C. H. B.

Effect of Phosphate-manuring on the Amount of Sugar, and the Value of Beet-root. By M. MAERCKER (*Bied. Centr.*, **21**, 804—808; from *Der Landwirth*, 1892, Nos. 66, 67, and 68).—Experi-

ments were made in which beet-root was grown in soil manured with 36—40 lbs. of phosphoric acid per morgen (63—70 lbs. per acre), with 14—18 lbs. per morgen (25—32 lbs. per acre), and without the application of phosphates. The soil was a normal beet-root soil—a mild loam generally over marl. The results, as regards sugar, gave practically no difference in favour of phosphoric acid. There was also no great difference in the yield of roots, although, the year (1891) being exceptionally favourable, a correspondingly large amount of phosphates would be required.

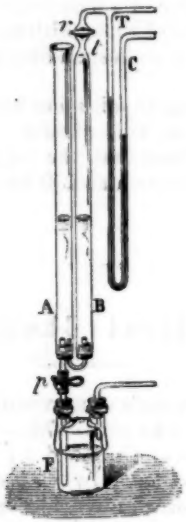
The mechanical properties of soil seem undoubtedly to be improved by phosphatic manuring, but this should be effected in a less costly manner. The results indicate that the large amounts of phosphoric acid sometimes applied (as much as 140 lbs. per acre being sometimes given) are excessive. N. H. M.

Analytical Chemistry.

New Accessory to Lunge's Gas-volumeter. By J. A. MULLER (*Ann. Chim. Phys.* [6], **24**, 570—574).—When it is required to measure the air or nitrogen displaced by a gas or vapour, as in the determination of vapour density by V. Meyer's method, or the volumetric estimation of carbonic anhydride in carbonates by Scheibler's process, and in all cases where the volume of the generating vessel is very great as compared with that of the gas to be measured, the displaced gas cannot be collected over mercury on account of the high specific gravity of the latter, but must first be collected over water. It is pointed out, however, that the volume of the displaced gas often differs, by reason of variations of temperature and pressure during the experiment, from that of the vapour or gas generated. For example, during the decomposition of a mixture of alkali carbonate and hydroxide by hydrochloric acid heat is developed, and it is necessary to wait about an hour for the reaction flask to attain an equilibrium of temperature. If now the surrounding temperature and pressure have varied in an opposite direction, the volume of the collected gas may vary from that of the liberated carbonic anhydride. To obviate this cause of error, there is placed by the side of the generating apparatus a vessel of like capacity full of air; the difference between the pressure of this air and that of the atmosphere is indicated by a water manometer. The arrangement shown in part below permits this difference to be determined, so that the error it gives rise to can be eliminated by increasing or diminishing the pressure at the end of the experiment.

A and B are two glass tubes of about 2 cm. diameter and 40 cm. in length; they are in communication at the lower ends. The manometer, attached to T, is half filled with coloured water. A and B are filled with water by opening the tap *t* and the pinchcock *p*, and compressing the superincumbent air in F by a caoutchouc bladder; when

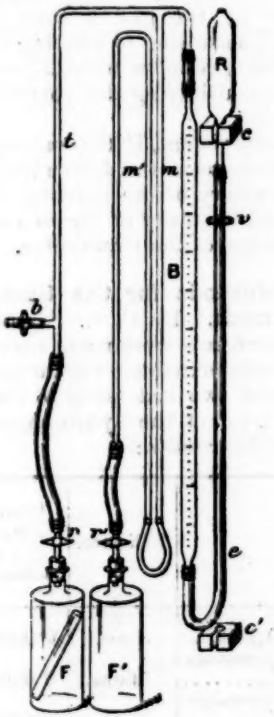
the generating apparatus and the vessel containing air (mentioned above) have attained a constant temperature, they are connected with the tubes T and C respectively. The gas to be measured is then



passed into the tube B, and the water allowed to flow out at the same rate by opening *p*. If the indication of the manometer C is not the same at the termination of the experiment as at the commencement, the equilibrium is restored by raising or depressing the level of the water in A. After this, the tap *r* is closed, the generating apparatus and the other vessel disconnected from T and C, and the gas passed into a Lunge's gas-volumeter at a constant temperature to be measured. A. R. L.

New Gas-volumeter. By J. A. MULLER (*Bull. Soc. Chim.* [3], **7**, 507—511).—The apparatus figured below serves for the measurement of gases evolved by reactions which take place at the ordinary temperature. It is composed of two vessels, F and F′, having each a capacity of 500 c.c.; they are fitted with singly bored india-rubber stoppers through which pass tubes fitted with taps *r* and *r*′. F communicates with the burette by the tube *t*. The upper portion of *t* is attached to one of the branches of the water manometer *m*, the other branch *m*′ communicating with F′. The burette B has a capacity of 500 c.c., and is divided into tenths from the upper portion downwards. The lower portion of the burette is attached by a stout caoutchouc tube *e* to a reservoir R, holding 60—70 grams of mercury. The small tube *b* is furnished with a piece of caoutchouc tubing and a screw clamp. The whole apparatus is fixed in a small cupboard which is only opened to perform the necessary manipulations or readings. More-

over, in order to ensure that the two vessels F and F′ are as near as possible of the same temperature, they are covered with a thick metal box which is readily taken to pieces.



The apparatus may have been thus left over night in a room in which the temperature has varied slightly, care having been taken to previously withdraw the plugs of the taps r and r', and to raise the mercury to the zero point of the burette. On the day following, the plugs of the taps are replaced, and the air shut up in the apparatus at a known temperature and pressure. The volume of the latter at 0° and 760 mm. will, when it is dry, be $V = \frac{P}{760 \times (1 + \alpha t)}$, or, when it is moist, $V = \frac{P - f}{760 \times (1 + \alpha t)}$, f being the tension of aqueous vapour at $t°$, and α the coefficient of expansion of the gas.

F is now charged with the necessary reagents, the taps closed, and the reaction started by inclining F. When the reaction is complete, the mercury reservoir is lowered and suspended in the lower holder c'. The tap r is now slightly opened, the clamp v loosened, the operator being guided in this portion of the operation by the levels of the water in the manometer. When these levels are again at the same

height, the clamp v is tightened. The reaction flask is agitated, and the apparatus allowed to remain for several hours. The tap r' is then opened, and the mercury in the burette is caused to ascend or descend, so as to readjust the level of the water in the manometer. The volume of the gas is then read off. This value multiplied by V or V′, according to whether the gas is dry or moist, gives the volume of the gas under normal conditions; the weight of the gas is obtained by multiplying this volume by the weight of 1 c.c. of the dry gas.

In making a fresh experiment, if the surrounding temperature and pressure are not the same as in the determination of the constants V and V′, it will be necessary before starting the reaction to aspirate out or force in a small quantity of air to readjust the level of the water in the two branches of the manometer. A. R. L.

Comparison of Methods for the Standardisation of Acid and Alkaline Solutions. By C. L. Parsons (*J. Anal. Chem.*, **6**, 372—375).—The experiments were made with an approximately N/5 hydrochloric acid and approximately decinormal ammonia and barium hydroxide solutions, the two last being so made that 2 c.c. of either should exactly equal 1 c.c. of the hydrochloric acid. The following table is a summary of the results:—

Method.	Indicator.	Grams NH_3 in 1 c.c. solution.	Grams HCl in 1 c.c. solution.	Grams $Ba(OH)_2$ in 1 c.c. solution.
By precipitation as $(NH_4)_2PtCl_6$ ..	—	0·001545	0·006634	—
By neutralisation with potassium tetroxalate.....	litmus	0·001560	0·006698	—
By neutralisation with potassium hydrogen tartrate	litmus	0·001564	0·006716	—
By precipitation as AgCl	—	0·001558	0·006679	0·007822
By pure pulverised Iceland spar..	cochineal	0·001567	0·006728	0·007880
By distillation of NH_3 from NH_4Cl	cochineal	0·001563	0·006717	0·007866
By precipitation as $BaSO_4$.....	—	—	0·006676	0·007820
By neutralisation with potassium tetroxalate	phenol-phthalein	—	0·006722	0·007875

It will be seen that in every case the figures obtained by gravimetric methods are lower than those obtained by volumetric methods. The estimations obtained by silver chloride and barium sulphate agree closely. Those by ammonium platinochloride are lower, as would be expected from the comparatively greater solubility of the salt. Taking convenience also into account, the silver chloride is undoubtedly the best of the gravimetric methods of standardisation. The author then discusses the volumetric methods, and concludes by saying: "The determinations made by the aid of potassium tetroxalate are almost exactly the average of all the results, both gravimetric and volumetric, and are, in my opinion, the most accurate."

A. J. G.

Potassium Tetroxalate for Akalimetry. By C. L. Parsons (*J. Anal. Chem.*, **6**, 375—380).—Many samples of commercial potassium tetroxalate prove, on examination, to be mixtures of the tetroxalate with varying quantities of potassium hydrogen oxalate; this fact probably explains why such varying opinions have been expressed as to the suitability of potassium tetroxalate as a standard for alkalimetric work. Pure potassium tetroxalate, $KHC_2O_4,H_2C_2O_4 + 2H_2O$, is prepared either from potassium carbonate and oxalic acid or from the commercial salt. Oxalic acid is added to a boiling solution of the salt, the heating continued for an hour, and the liquid allowed to cool, when the salt separates in well formed crystals, which are washed once by decantation with water, and recrystallised several times from pure distilled water. The crystals are then pressed between filter paper and dried for 12 hours over sulphuric acid. The salt thus obtained, although containing water of crystallisation, is perfectly stable in air.

For titration against solutions of the fixed alkalis, phenolphthaleïn is the best indicator; for ammonia solutions, litmus must be employed, the point taken being the distinct appearance of the blue colour, which is sharp and unmistakable. A. J. G.

Employment of Borax for standardising Acids. By E. Rimbach (*Ber.*, **26**, 171).—The author recommends the employment of borax in place of sodium carbonate for standardising normal acids, methyl-orange being used as indicator, which, from the observations of Joly (Abstr., 1885, 440) and the author, is shown to be unaffected by boric acid. The author's investigation of the atomic weight of boron (this vol., ii, 207) shows that the method gives accurate results, and the salt has the advantage over sodium carbonate that it is more readily obtained pure, and that, owing to its high molecular weight, errors in weighing only affect the results to one-fourth the extent they would with sodium carbonate. For ordinary purposes, it is sufficient to recrystallise commercial borax two or three times, and allow it to remain in the air for two or three days with frequent turning over. 1 gram of crystallised borax, weighed in the air with brass weights, is equivalent to 5·2391 c.c. of normal acid, or 1 litre of normal acid corresponds with 190·872 grams of crystallised borax weighed under similar conditions. H. G. C.

Detection of Hydrogen Peroxide. By G. Griggi (*L'Orosi*, 1892, 295—296).—The rapid disappearance of the blue colour of the ethereal extract of an aqueous solution of chromic anhydride and hydrogen peroxide may be avoided by substituting amyl alcohol for the ether. On shaking the solution of chromic anhydride and hydrogen peroxide with an equal volume of amyl alcohol, the latter acquires a magnificent indigo colour, which retains its original intensity for six hours at 24°. W. J. P.

Estimation of Chlorine in Wine. By A. Solaro (*Staz. Sper. Agrar.*, **21**, 154—162).—Comparative experiments on the estimation of chlorine in wine were made, using the methods of Tony-Garcin as

modified by Dujardin, Roos (*Staz. Sper. Agrar.*, **18**, 758), and of Sinibaldi and Combe (*ibid.*, **20**, 635). For the experiments, two samples of wine were employed: to one, 0·2 per cent. of pure sodium chloride was added; to the other, 0·1 per cent. Determinations of chlorine in the ash from 100 c.c. of wine gave the percentage results 0·2078 and 0·1064 respectively. Dujardin's method gave very high results. Roos' method gave much better results, but generally rather low. Sinibaldi and Combe's method gave results almost identical with those obtained by Roos' method. Very good results are obtained as follows:—The wine is decolorised with animal charcoal, and 20 c.c. of the filtered liquid poured into a 50 c.c. flask, treated with a few drops of nitric acid, and an excess of N/20 silver solution; the volume is then made up to 50 c.c., and the whole shaken and filtered; to 25 c.c. of the solution, corresponding with 10 c.c. of wine, some more nitric acid and ammonium iron alum (0·5 c.c.) free from chlorides, are added; the excess of silver is then determined with N/20 ammonium thiocyanate; with wine No. 1, the highest and lowest results were respectively 0·2106 and 0·2061 per cent.; with No. 2, the results were 0·1199 and 0·1170 per cent. N. H. M.

Preparation of Standard Iodine Solution. By H. L. Payne (*Chem. News*, **66**, 286).—As a standard iodine solution alters on keeping for a long time, the author proposes a method whereby a litre of such a solution can be prepared in two minutes in any laboratory where a standard permanganate solution is constantly at hand. For this purpose, about 10 grams of potassium iodide is dissolved in a litre flask, and acidified with sulphuric acid; the calculated quantity of standard potassium permanganate is run in, and, after a few minutes, when the reaction is complete, the whole is diluted to the mark; a clear solution of known content of iodine is thus obtained, 5 atoms of iodine being liberated for each molecule of permanganate ($KMnO_4$). D. A. L.

Estimation of Fluorine in the Ashes of Plants. By H. Ost (*Ber.*, **26**, 151—154).—For the estimation of fluorine in vegetable ash, precipitation as calcium fluoride is out of the question, as it would be practically impossible to separate traces of calcium fluoride from such a complex mixture; under these circumstances the author employs the following method:—The ash from 15—20 grams of the air-dried substance is gently fused with silica (1½ parts) and fusion mixture (5 parts), the melt extracted with hot water, the filtered solution warmed with ammonium carbonate, kept for 12 hours, and again filtered to separate the silica, alumina, &c., the residue being washed with dilute ammonium carbonate. The solution is then evaporated until free from ammonia, almost neutralised with nitric acid, evaporated to dryness with a small quantity of a pure ammoniacal solution of zinc hydroxide, and the residue taken up with water; after filtering, the solution is again evaporated, the residue treated with water, the feebly alkaline filtrate, which is now free from ammonia and silica, heated to boiling, almost neutralised with nitric acid, and treated with calcium chloride. The precipitate is separated by filtration, evaporated with acetic acid in a platinum dish, and,

after completely expelling the acid, treated with water; the residue, which consists of calcium fluoride, calcium phosphate, and other substances, is placed in a platinum crucible, together with a few drops of sulphuric acid, the crucible covered with a weighed glass plate, and heated on a sand-bath, first at 100—150° for eight hours, and then more strongly, until sulphuric acid vapours begin to be evolved. The loss in weight of the glass cover is approximately proportional to the quantity of fluorine present, quantitative experiments with pure calcium fluoride having shown that 1 milligram of fluorine usually causes a loss in weight of 0·8 to 0·9 milligram.

Analyses of the ashes of the leaves of various plants, growing under healthy conditions, were made in this way, and in all cases a small quantity of fluorine (about 0·1 per cent.) was found; the results of quantitative experiments, in which a known weight of calcium fluoride was added to the plant ash before fusion, showed that 1 milligram of fluorine in the ash corresponds with a loss of about 0·5 to 0·6 milligram on etching. F. S. K.

The Gunning-Kjeldahl Method, and a Modification applicable in the presence of Nitrites. By A. L. WINTON (*Exper. Stat. Record*, **4**, 336; from *Conn. Stat. Bul.*, June, 1892).—The substance (0·5—1 gram) is digested for two hours with 30 c.c. of Sconell's salicylic acid mixture (sulphuric acid 30 c.c., salicylic acid 2 grams) in a 600 c.c. flask, being frequently shaken. Zinc-dust (2 grams) is gradually added, and the flask gradually heated to boiling. Potassium sulphate (12 grams) is now added, the boiling continued for a little while after the solution has become colourless (or is straw-coloured, as when iron is present). On cooling, as the whole begins to solidify, water is added, and the distillation with soda carried out in the usual manner. A table of results, obtained by the original method and by this modification, is given in the original paper. The greatest discrepancy is 0·1 per cent., and the average 0·05 per cent.

N. H. M.

Estimation of Phosphorus in Iron and Steel. By A. CARNOT (*Compt. rend.*, **116**, 106—108).—About 5 grams of good iron or steel (or 0·5 to 1·0 gram if impure) is dissolved in 40 c.c. of pure nitric acid, and, when effervescence has ceased, the solution is gently heated, mixed gradually with 2 c.c. of concentrated sulphuric acid for each gram of metal, and evaporated gradually to dryness, with repeated stirring. The residue is heated at 120—125° for two hours in order to make the silica insoluble, dissolved in about 50 c.c. of boiling water, and the solution filtered. The residue, after treatment with hydrochloric acid to remove any manganese oxide, will give an accurate estimation of silicon, as in Drown and Shimer's method.

The filtered solution is heated to boiling for about half an hour with 1 gram of chromic acid, in order to oxidise the organic matter, and at the same time convert any pyrophosphoric acid into orthophosphoric acid; 60—80 c.c. of a 5 per cent. molybdic solution, prepared in the usual way, is then added, and the liquid is heated at 100° for two or three hours. After cooling, the clear liquid is decanted off, and the precipitate washed with tepid water containing

5 per cent. of the molybdic solution. The precipitate is then dissolved in 30 c.c. of ammonia solution, diluted with an equal volume of water, and poured through the filter on to which the washings had been decanted. If any insoluble matter remains on the filter, it is dissolved in warm, dilute nitric acid, and added to the acid solution which will presently be mentioned. The ammoniacal solution of the precipitate is cooled and gradually neutralised with nitric acid, care being taken that the temperature does not rise above 40°. As soon as a permanent precipitate separates, 3 c.c. more nitric acid is added, and the liquid is heated at about 40° for two hours. The precipitate is first washed with dilute nitric acid (1 : 100), and afterwards with water, and is dried at 100° and weighed. The weight of phosphorus contained in it is found by multiplying by 0·01628.

Analysis shows that the ammonium phosphomolybdate formed under these conditions has the composition MoO_3, 90·720; P_2O_5, 3·688; $(NH_4)_2O$, 4·160; H_2O, 1·432 = 100·000, which agrees almost exactly with the formula $P_2O_5,24MoO_3,3(NH_4)_2O + 3H_2O$.

C. H. B.

Estimation of Phosphoric acid as Magnesium Pyrophosphate. By H. Neubauer (*Zeit. anorg. Chem.*, **2**, 45—50).—This method is not so trustworthy as is generally supposed. If the magnesium ammonium phosphate is precipitated in a solution containing free ammonia, together with more than a certain quantity of ammonium salts (as is the case when the phosphoric acid has been first precipitated as phosphomolybdate, then dissolved in ammonia, and reprecipitated with magnesia mixture) then the precipitate, when ignited, loses a small quantity of phosphoric acid. Probably some $Mg(NH_4)_4(PO_4)_2$ is precipitated along with the $MgNH_4PO_4$, and when ignited loses, amongst other things, P_2O_5, leaving $Mg_2P_2O_7$. That phosphoric acid is actually lost, was proved by covering the crucible with a lid coated with a thin layer of magnesium oxide; the lid increased in weight, and the coating could be shown to contain phosphoric acid at the end of the experiment.

Reasons are given for believing that a solution containing a known amount of phosphoric acid cannot accurately be made from either sodium phosphate or magnesium ammonium phosphate. The use of silver phosphate for this purpose is recommended. It is prepared by precipitation, purified by dissolving it in dilute nitric acid and reprecipitating with ammonia, gently ignited, and weighed. It is now dissolved in dilute nitric acid (any residue being collected, weighed, and its weight deducted from that of the silver phosphate), the silver is precipitated with hydrochloric acid, the filtered solution concentrated to drive off nitric and hydrochloric acids, and the residue diluted with water, filtered, and made up to a known volume. The weight of phosphoric acid in this volume = weight of silver phosphate taken × 0·1695.

C. F. B.

Precipitation of Phosphorus as Ammonium Phosphomolybdate in the presence of Arsenic. By H. C. Babbitt (*J. Anal. Chem.*, **6**, 381).—The author has made experiments on the estimation of phosphorus in steel by precipitation as ammonium phosphomolybdate, and

finds that if the temperature of precipitation is kept at or below 25° the presence of arsenic has no influence on the accuracy of the phosphorus determinations, but at temperatures above 25° arsenic is precipitated in amounts that increase rapidly with the temperature.

A. J. G.

Citrate and Molybdate Methods for the Estimation of Soluble Phosphoric acid. By M. MAERCKER (*Landw. Versuchs-Stat.*, **41**, 329—373).—The paper is a report on comparative experiments made by the two methods at various German experimental stations and by representatives of manure manufacturers. A solution containing a known amount of phosphates was made, and samples distributed for analysis. With a view to avoid errors, the amounts actually analysed were in each case weighed instead of measured. Tables of the results obtained at the various stations are given. The greatest deviation from the average (0·1639 gram, using 50 grams of solution) was 1·6 milligrams by the molybdate, and 1·7 milligrams by the citrate method; or, as 1 milligram corresponds with 0·1 per cent. of the superphosphate employed, the greatest deviation would be $\pm 0{\cdot}16$ and $\pm 0{\cdot}17$ per cent. respectively. The results obtained by the various analysts generally agreed very well, but, taking all together, the results are not considered quite satisfactory, and it was decided to repeat the experiment.

In one case, a difference was noticed in molybdate precipitates which had been left 12 and 24 hours respectively after the mixture of superphosphate and molybdate had been kept for nearly half an hour. In the first case (which gave an average result of 0·1266 gram $Mg_2P_2O_7$), the precipitate was pure white; in the second case (average result 0·1286 gram), the precipitate was grey-white or grey-blue. The lower results with the white precipitate were probably the best.

A solution of pure sodium phosphate was next made, and, after its strength had been determined by evaporating to dryness and also by precipitation with magnesia mixture (by both methods, 50 grams was found to contain 0·1676 gram of P_2O_5), 50 grams of a solution containing pure iron (2·94 grams), pure alumina (2·24 grams), and pure calcium carbonate (43·90 grams per litre, dissolved in nitric acid) was added to every litre of the phosphate solution. On analysis, an absolutely correct average result was obtained. The citrate method gave on the average 0·0007 gram too much, and the greatest difference between the two methods was 1·4 milligrams of phosphoric acid. The citrate method was, therefore, unhesitatingly declared to be trustworthy.

Direct Estimation of Nitrogen in Chili Saltpetre.—Comparative experiments were made with the Jodlbauer, aluminium, and zinc-iron (Kühn) methods. It was decided that all three methods (the aluminium method being modified) are good, but Kühn's method was recommended on account of the ease and quickness with which it is worked. The method is as follows:—The nitrate (10 grams) is dissolved in water (1 litre), and 50 c.c. of the filtered solution put with water (120 c.c.) and aqueous soda (1·3 sp. gr., 80 c.c.) in an Erlenmeyer flask of 750 c.c. capacity. Zinc-dust (5 grams) and powdered iron (*ferrum limatum pulv.*, 5 grams) are then added, the

flask connected with a condenser, and the whole left for one hour. About 100 c.c. is then quickly distilled off into acid. A sketch of the apparatus is given, by means of which six distillations can go on at once. The flasks are provided with suitable bulbs to prevent the splashing over of any soda. The condensing tubes are of tin. The ends of the condenser do not dip into the acid, but the receivers are provided with safety tubes containing acid (the same as that in the receivers), which is eventually washed back into the flasks.

Decomposition of Basic Slag by means of Hydrochloric acid and of Sulphuric acid.—The results of several experiments in which hydrochloric acid and sulphuric acid respectively were used were decidedly against the use of the former acid, which, under some conditions, gives too high results. It was therefore decided to use sulphuric acid. The formation of crusts is avoided by adding a little sand to the acid; this causes the acid liquid to boil with more motion.

N. H. M.

Estimation of Phosphoric Anhydride in Basic Slag. By G. Mancuso-Lima (*Staz. Sper. Agrar.*, **21**, 225—228).—The finely powdered slag (2 grams) is put into a flat dish and treated with sulphuric acid (25 c.c.) diluted with half its volume of water, stirring quickly with a glass rod; the pasty mass thus formed is left for about two hours, treated with warm water, filtered, and washed. Milk of lime free from phosphates is then added, the whole shaken, and, when alkaline, it is heated for about half an hour on a water bath, treated with nitric acid until the lime precipitate is redissolved, allowed to cool, and filtered. The solution is precipitated with ammonium molybdate, and the analysis continued in the usual manner. The method was compared with Olivieri's method, with that proposed by Martinotti, and with the Italian official method, a mixture of known composition, containing sodium phosphate (5 grams), iron (2 grams), manganese (2 grams), and potassium silicate (1 gram) being employed. With the exception of the official method, which gave results nearly 50 per cent. too low (owing to the formation of basic iron phosphate), the different methods gave fairly concordant results: Olivieri, 0·8605; Martinotti, 0·8948; and Mancuso, 0·830 gram. The actual amount was 0·835 gram. The three methods were then tried with the same slag, Martinotti's method being slightly modified in order to save time. Two grams of the slag was treated with 20 c.c. of strong hydrochloric acid and evaporated to dryness on a water bath; this operation was repeated, after which the residue was treated with fuming hydrochloric acid, dissolved in water, and made up to 100 c.c.; 50 c.c. of this was treated with ammonium citrate (120 c.c.) and ammonia (30 c.c.); 100 c.c. was then precipitated with magnesia mixture. The results were all very similar. The author prefers his method as being quicker. N. H. M.

Estimation of Phosphoric Anhydride in Basic Slag. By D. Martelli (*Staz. Sper. Agrar.*, **21**, 453—455).—The author has compared the methods of Martinotti (*Staz. Sper. Agrar.*, **19**, 614), Olivieri (*ibid.*, **20**, 159), and Mancuso-Lima (preceding abstract)

with that given by König in his *Untersuchung landw. und gewerbewichtiger Stoffe* (Berlin, 1891, pp. 178—179, and 163). He considers the methods described by König to be the best, as effecting a saving both of time and reagents. N. H. M.

Eschka's Process for the Estimation of Sulphur. By F. Hundeshagen (*Chem. Zeit.*, **16**, 1070—1071).—Eschka has recommended igniting coal with a mixture of sodium carbonate and magnesium oxide, whereby the sulphur is converted into sodium sulphate. The author, however, has noticed that, even with the greatest care, there is an appreciable loss of sulphur, sometimes as much as 6 per cent. of the total amount. In fact, when analysing samples of coal rich in sulphur, part of this escapes as hydrogen or ammonium sulphide, easily detectible by lead paper.

If, however, potassium carbonate is used instead of the sodium compound, no loss of sulphur need be feared. The author now proposes the following plan:—A mixture is prepared, consisting of 2 parts of magnesium oxide and 1 part of calcined potassium carbonate. For 1 part of coal, 2 parts of this mixture are used, three-fourths of which is intimately mixed with the coal, whilst the remainder is sprinkled on the top. The operation seldom takes more than half an hour. The test analyses are satisfactory.

L. de K.

Influence of the Sulphur contained in Coal Gas on the Estimation of Sulphur by Fusion. By J. D. Van Leeuwen (*Rec. Trav. Chim.*, **11**, 103—105).—The best fusing mixture is stated to be that recommended by Böckmann, namely, potassium chlorate (1 part) and sodium carbonate (6 parts). The author's results confirm those obtained by others, that, by employing a coal-gas flame for the fusion, the percentages of sulphur found are too high. A. R. L.

Gravimetric Estimation of Sulphuric acid. By M. Ripper (*Zeit. anorg. Chem.*, **2**, 36—44).—The usual method is vitiated by the fact that the precipitated barium sulphate carries down other matters, notably potassium salts, with it, and these are not readily removed by washing; and also by the fact that, when ignited with the filter paper, some of the sulphate is reduced to sulphide. When the total amount of sulphate is small, the consequent error may even reach 20 per cent. of the whole; if the modifications described below be adopted, it does not exceed 0·3 per cent. The washed precipitate is brought, whilst still moist on the filter, into a platinum crucible, and there burned. The ash is then treated with bromine water drop by drop, till the red colour of the bromine is permanent; by this means any sulphide that may have been formed is reconverted into sulphate. Another drop or two of bromine water and 10—15 c.c. water are now added, the whole is heated on the water-bath until the bromine has been driven off, 2—3 drops of hydrochloric acid are added, and the warming continued for 10 minutes. The precipitate in the crucible is now washed several times by decantation, the wash-water being poured off through a small filter; other substances carried down with the barium sulphate

are thus removed. The filter is placed in the crucible, the whole ignited, and the residue treated with a drop of bromine water, or of dilute sulphuric acid, again ignited, and weighed. C. F. B.

Volumetric Estimation of Sulphuric acid in Sulphates. By A. v. Asbóth (*Chem. Zeit.*, **16**, 922).—The author has tried the process recommended by Stolle (compare this vol., ii, 188), but has found that a solution of barium chromate in dilute hydrochloric acid does not keep, but rapidly decomposes, and will then, after addition of ammonia, contain barium chloride. Experimenting on pure potassium sulphate, using a barium chromate solution 24 hours old, the author only found 87 per cent. of K_2SO_4; and when using a five days old solution, the percentage fell to 55·1 per cent. With a freshly-prepared solution, good results may probably be obtained. L. de K.

Estimation of Carbonic Anhydride in the Air of Buildings. By A. H. Gill (*Analyst*, **17**, 184—186)—The air to be tested is drawn into a bottle by means of bellows. The bottle, which should be perfectly clean and dry, should hold 4 or 8 litres, and be fitted with a rubber stopper carrying a glass tube closed by a small, unperforated rubber nipple. 50 c.c. of standard barium hydroxide is run in rapidly from a burette, the tip passing entirely through the tube in the stopper; the nipple is replaced and the solution spread completely over the sides of the bottle, while waiting three minutes for the draining of the burette before reading. The bottle is now placed upon its side, and shaken at intervals for 40—60 minutes. At the time when the baryta is added, the temperature and pressure should be noted. At the end of the above period, the bottle is well shaken, the cap is removed from the tube, and the bottle is quickly inverted over a 50 c.c. glass stoppered bottle, so that the solution shall come in contact with the air as little as possible. Without waiting for the bottle to drain, 15 or 25 c.c. of the baryta water is withdrawn with a pipette, and at once titrated with sulphuric (not oxalic) acid, using rosolic acid as indicator. The acid is made of such a strength that 1 c.c. equals 1 milligram of carbonic anhydride; therefore the difference in the number of c.c. of acid required to neutralise 50 c.c. of baryta water before and after absorption gives the number of milligrams of carbonic anhydride in the bottle.

In very correct analyses, notice should be taken of the amount of moisture present in the air. L. de K.

Estimation of Rubidium by the Spectroscope. By F. A. Gooch and J. I. Phinney (*Amer. J. Sci.*, **263**, 392—400).—Gooch and Hart (Abstr., 1892, 913) have successfully estimated small quantities of potassium by means of the spectroscope. The authors have endeavoured to apply the idea to the estimation of rubidium. Sodium was, curiously enough, found to increase the brightness of the potassium line, and now it seems that it also remarkably increases the brightness of the rubidium line. Potassium has an effect similar to that of sodium. Too large proportions of either sodium or potass-

ium chloride are however injurious, but may be got rid of by precipitation with alcohol.

Whilst the estimation of potassium gave very satisfactory results, the errors introduced when estimating rubidium are manifestly large; but if the question is the estimation of only a few milligrams of the metal, the authors think that for want of a better process, the spectroscopic test may prove of some value. L. DE K.

Estimation of Calcium in Basic Slag. By A. F. HOLLEMAN (*Chem. Zeit.*, **16**, 1471—1472).—The author has found that when estimating lime in a ferruginous substance, like basic slag, a combination of Classen's and Jones' methods should be employed. 50 c.c. of the solution, containing 1 gram of sample, is concentrated to a small bulk, and then mixed with 20 c.c. of a solution of potassium oxalate (1—3). After digesting on the water-bath for about 10 minutes, the calcium oxalate is collected, and washed with hot water until the washings are free from oxalate. The precipitate is now washed off the filter, and then dissolved in 15 c.c. of hydrochloric acid. To avoid loss, the filter must also be rinsed with a little weak acid. After evaporating down to 25 c.c., 10 c.c. of dilute sulphuric acid (1—5) is added, and then 150 c.c. of alcohol. After a few hours the calcium sulphate is collected on a filter and washed with alcohol until the washings give no colour with methyl-orange. The sulphate is then heated, with the usual precautions, to constant weight. The test analyses prove the remarkable accuracy of the process.

L. DE K.

Quantitative Separation of Strontium and Calcium Nitrates by means of Amyl Alcohol. By P. E. BROWNING (*Amer. J. Sci.*, **266**, 462—463).—The author (compare Abstr., 1892, 916) recommended boiling about 0·5 gram of the mixed nitrates with two successive portions of 30 c.c. of amyl alcohol. He now states that 10 c.c. each time is quite sufficient, which lessens the allowance for the solubility of strontium nitrate. L. DE K.

Quantitative Separation of Barium and Strontium by the action of Amyl Alcohol on their Bromides. By P. E. BROWNING (*Amer. J. Sci.*, **264**, 459—462).—The author has found that 10 c.c. of amyl alcohol dissolves only an amount of barium bromide equivalent to 0·0013 gram of barium oxide; whilst, in the case of calcium, as much as 0·2 gram is dissolved. The author has founded on this fact an excellent method for separating the two metals, the *modus operandi* being very similar to the one previously described (compare Abstr., 1892, 915). After the bromides have been separated by the amyl alcohol, they cannot be conveniently weighed as such, but must be converted into sulphates. The amylic solution of the strontium may be precipitated at once with sulphuric acid, after adding sufficient alcohol to get a convenient mixture. As the barium bromide is not quite insoluble, the weight of the barium sulphate will be a trifle too low, whilst that of the strontium will be a little too high; the necessary correction, therefore, has to be made. L. DE K.

Detection and Estimation of Minute Quantities of Lead in the presence of Copper and Iron. By F. L. Teed (*Analyst*, **17**, 142—143).—The most delicate reaction for both lead and copper is, no doubt, ammonium sulphide, and the amount present can, of course, be estimated colorimetrically by comparison with known quantities. The objection to the use of ammonium sulphide is, however, that it does not distinguish between the two metals. To effect this distinction, the author makes use of the well-known fact that copper is not affected by ammonium sulphide in presence of potassium cyanide. To test for lead in lemonade, for instance, a measured quantity of the liquid is placed in a cylinder or white basin, and after adding a few c.c. of ammonia, mixed with a few drops of solution of potassium cyanide. If now a drop of ammonium sulphide is added the lead is precipitated, but not the copper or iron.

Lead may also be detected, but not estimated, in tartaric acid by burning this substance and digesting the ash with strong sulphuric acid, which will, of course, convert any lead into sulphate and dissolve it; the author discovered, some years ago, a most delicate test for lead in sulphuric acid, consisting in adding a drop of hydrochloric acid, or a crystal of common salt. Any lead is precipitated as chloride, giving a peculiar pearly opalescence. L. de K.

Volumetric Estimations and Separations by means of Potassium Ferrocyanide and Ferricyanide. By C. Luckow (*Chem. Zeit.*, **16**, 1428—1429; 1449—1450).—The author (compare Abstr., 1892, 1129, 1527) gives numerous instances where his process is useful for the quantitative estimation of a mixture of metals. As an example may be quoted the estimation of the constituents of an alloy of copper (5 per cent.), antimony (10 per cent.), and tin (85 per cent.). 1·2 grams of the alloy was dissolved in 12 c.c. of a mixture of 3 vols. of hydrochloric acid (sp. gr. 1·12) and 1 vol. of nitric acid (sp. gr. 1·2), with the aid of a gentle heat. Potassium chlorate was now added until the liquid had, even after 10 minutes, a decided odour of chlorine, showing that all the antimony had passed into the highest state of oxidation. After cooling and adding a little solution of tartaric acid, the mixture was put into a 100 c.c. flask, the beaker rinsed with some more tartaric acid, and the whole made up to the mark. 25 c.c. of this solution (= 0·3 gram alloy) was mixed with 10 c.c. of dilute sulphuric acid (1—10), and the copper was roughly titrated with a solution of potassium ferricyanide, 1 c.c. of which represented 0·00474 gram of Cu. The experiment was now, of course, repeated, and it was found that, after making an allowance of 0·4 c.c., 3·3 c.c. of ferricyanide was required, which gave 5·2 per cent. of copper instead of 5 per cent. 10 c.c. of the solution (= 0·12 gram alloy) was mixed with 10 c.c of dilute sulphuric acid, and then with 8 c.c. of a solution of potassium ferrocyanide, 1 c.c. of which represented 0·0118 gram of Sn. After slightly warming for three minutes, the liquid had completely gelatinised. On adding 0·2 c.c. more ferrocyanide at the time, it was found that the iron test made its appearance when 9 c.c. had been used. The experiment was now most carefully repeated, 8·5 c.c. ferro-

cyanide being straightway added, and then further additions of 0·2 c.c. were made. It was found that the reaction was complete when 8·8 c.c. was used, and after allowing 0·1 c.c. this made 8·7 c.c., which calculated to metal gave 85·5 instead 85 per cent. of tin. If the antimony was simply taken from the difference, the analysis only took an hour, but a direct estimation was also performed as follows:—50 c.c. of the solution was mixed with a decided excess of potassium ferrocyanide. After filtering and washing the precipitate with weak brine, the antimony was precipitated with hydrogen sulphide, the precipitate dissolved in sodium sulphide and then electrolysed. 9·4 per cent. of antimony was obtained.

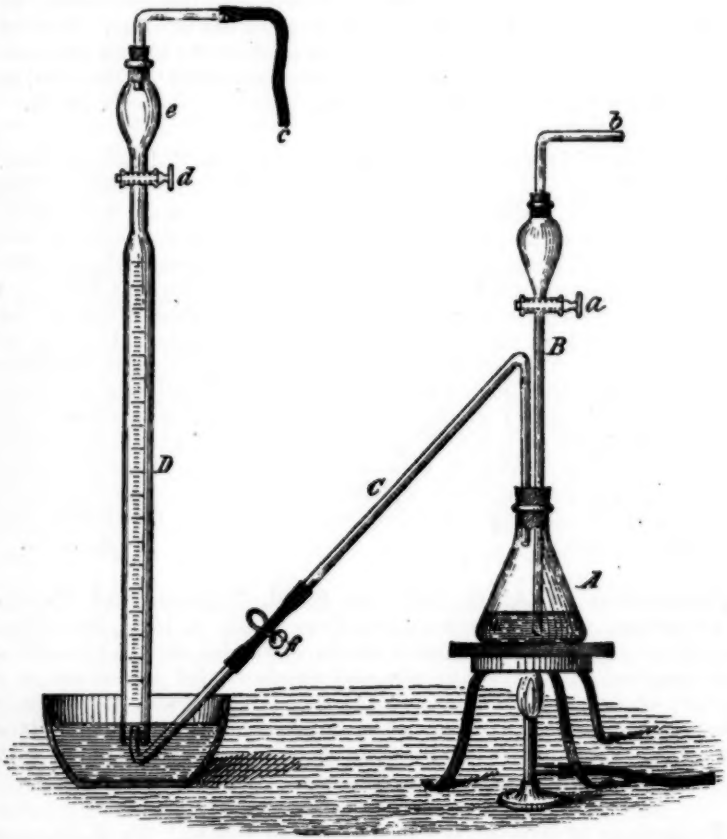
With a little ingenuity, the process described by the author may be so altered as to suit the assay of almost any kind of alloy. For the benefit of those who might like to try the method, the author has constructed a very useful table, showing the properties of the various metallic ferrocyanides and ferricyanides. L. DE K.

Detection of Mercury in the Organism. By E. LUDWIG (*Chem. Centr.*, 1892, ii, 941; from *Pharm. Post*, **25**, 1099—1101).—The organs are finely divided, weighed, and boiled for some hours with an equal weight of 20 per cent. hydrochloric acid, then cooled to 60°, and potassium chlorate added in portions of half a gram, whereby the dark liquid becomes clear; it is then cooled, thrown on a filter, the residue washed with water, and 5 grams of zinc dust added to the filtrate, which is then vigorously stirred for five minutes. It is kept for some hours with repeated agitation and a second portion of zinc dust is then added with vigorous stirring. The zinc is allowed to settle, the clear liquid poured off, the residue washed, first with water, then with the addition of a few drops of aqueous soda, and finally again with water. The residue is collected on a glass wool filter, treated with alcohol to remove water, and dried by suction in a stream of air. The mercury is then separated from the zinc dust by distillation and recognised as usual. A. J. G.

Estimation of Aluminium in Steel, Bronze, and Ferro-aluminium. By P. ROZYCKI (*Chem. Centr.*, 1892, ii, 1047; from *Mon. Sci.*, **6**, ii, 815).—0·2 to 2 grams of the finely divided alloy is placed in a platinum boat in a porcelain tube, and slowly heated to redness in a current of oxygen. When the oxidation is completed, the mass is ignited in a current of hydrogen chloride, when only the alumina, mixed with silica, remains. The silica can be removed by treatment with hydrofluoric acid and subsequent ignition. A. J. G.

Behaviour of Ferric Oxide in Soil and Rocks. By R. SACHSSE and A. BECKER (*Landw. Versuchs-Stat.*, **41**, 453—466).—Ferric oxide (not as silicate) in soils can be estimated by reducing with hydrogen, and measuring the hydrogen which is evolved by the action of the reduced iron on an acid. The substance containing iron is weighed in a platinum boat, the boat put into a wide glass tube and heated in a stream of hydrogen. While this is going on, water is boiled in the

flask *A* (see fig.) to drive out the air; when the reduction of the ferric oxide is complete, the boat is slipped out of the tube into the flask without interrupting the hydrogen evolution. The flask is closed with a cork provided with a funnel tube, *B*, and a delivery tube, *C*; the tap *a* is opened, and the tube *b* connected with a carbonic anhydride apparatus from which carbonic anhydride is passed into *A* until all the air is displaced. The end of the tube *C* is now placed under the measuring tube *D*, and the clamp *f* and the tap *a* closed. The funnel is filled with dilute, boiled sulphuric acid, the cork of *b* replaced and connected with the carbonic anhydride apparatus. The burner under



A is lighted and acid let in. By continued boiling all the hydrogen is driven into *D*. The measuring tube is then placed in a tall cylinder of water, the volume of gas read and reduced to 0° and 760 mm.

If the substance analysed contains silicates, these may be partly

decomposed with formation of ferric sulphate. This will redissolve a part of the metallic iron and yield ferrous oxide. In this case the contents of the flask are cooled in an atmosphere of carbonic anhydride, made up to 500 c.c., of which 250 c.c. is quickly filtered and titrated with permanganate. Some silicates, such as the micas, give ferrous oxide with hot dilute sulphuric acid. A correction for this is made by making one or more determinations without previously reducing with hydrogen.

Good results were obtained with pure ferric oxide; the introduction of ferric oxide with the sulphuric acid had no injurious effect. Good results were also obtained with ferric oxide mixed with biotite. With laterite and with two red soils no results could be obtained which were at all concordant; this was not due, as was shown by direct experiments, to the presence of hydrated silica, nor was sufficient organic matter present to account for the great differences. By prolonged heating of the red soil practically the whole of the ferric oxide disappeared. This can only be explained by the assumption that the ferric oxide was found in the soil as hydrated silicates or iron-kaolin; this would be reduced by hydrogen, but by ignition would be rendered difficultly decomposable.

Both ferric and ferrous oxides (especisly ferrous) when ignited with hydrated silicates partly decompose, becoming at the same time converted into silicates. This was shown to be the case by heating mixtures of ferric oxide with kaolin, apophyllite, and analcime respectively; with eläolite the reaction did not take place, and the whole of the iron was removed. N. H. M.

Detection of Gold in Dilute Solution. By T. K. Rose (*Chem. News*, **66**, 271).—The purple of Cassius reaction may be successfully applied in a test-tube to detect gold in solutions containing as little of this metal as 1 in 4,000,000, whilst with more dilute solutions, by employing a greater bulk of liquid (3 litres or so) and pouring it, when heated to boiling, into a large beaker containing 10 c.c. of a saturated aqueous solution of stannous chloride, acidified with hydrochloric acid, so as to mix the two liquids as rapidly as possible, a distinctly purple precipitate has been obtained with a 1 per 100,000,000 solution. The reaction is not disturbed by the presence of sodium chloride, calcium sulphate, potassium chloride, potassium bromide, or ammonium chloride, either separately or all together; it may be applied, therefore, for testing sea water for gold precipitable by stannous chloride. D. A. L.

Volumetric Estimation of Sulphates in Potable Waters. —By D. Vitali (*L'Orosi*, 1892, 260—262).—The volumetric process devised by the author for estimating the metals of the alkaline earths (Abstr., 1892, 1521) is applicable in a reversed form to the determination of dissolved sulphates. A known volume of N/10 barium chloride solution is added to the liquid to be titrated, the barium sulphate filtered off, and one-half of the volume of the liquid before filtration collected. The excess of barium in this is then found by titration with N/10 sodium carbonate solution as described in the paper above

mentioned. The solution must be neutral and, of course, free from substances which precipitate barium.

For the estimation of sulphates in potable waters, 500 c.c. of the boiling water is made alkaline with sodium carbonate solution; after filtration, the filtrate and washings are evaporated to 50 c.c., and the boiling solution accurately neutralised with acetic acid. 25 c.c. of N/10 barium chloride solution is now added and the solution filtered; one-half the previous volume of the solution is collected and the excess of barium estimated by titration with sodium carbonate solution. No allowance is made for the volume of the barium sulphate precipitate. W. J. P.

Cyanogen Iodide and Sodium Thiosulphate. By C. Meineke (*Zeit. anorg. Chem.*, **2**, 157—164).—E. v. Meyer (Abstr., 1888, 242) stated that cyanogen iodide is decomposed by hydrogen iodide and by sulphurous acid, and proposed to make use of these reactions for the volumetric estimation of cyanogen iodide. He did not, however, adduce experimental proof, but this is now brought forward by the author as regards the more complicated reaction between cyanogen iodide and sodium thiosulphate. A known weight of cyanogen iodide, dried over sulphuric acid and subsequently sublimed at the lowest possible temperature, was dissolved in a known weight of water, and potassium iodide (1 gram) and hydrochloric acid (sp. gr. 1·12; 1 c.c.) added to weighed quantities of the solution, containing 0·3—0·4 gram of cyanogen iodide; the liberated iodine was then estimated by ascertaining the weight of a standard solution of sodium thiosulphate required to reduce it. The results obtained were in accordance with the equation $2CNI + 4Na_2S_2O_3 + 2HCl = 2Na_2S_4O_6 + 2NaCl + 2NaI + 2HCN$. In neutral solutions, however, cyanogen iodide (3 mols.) reacts with sodium thiosulphate (5 mols.), giving rise to sodium sulphate (1 mol.). The author believes that the last-named salt is produced by a secondary reaction between the alkali cyanide and tetrathionate.

Potassium cyanide may be titrated with standard acid and methyl-orange, the liberated hydrogen cyanide being without action on the indicator. A. R. L.

Estimation of Cyanogen in Iodine. By C. Meineke (*Zeit. anorg. Chem.*, **2**, 168—174).—The author finds that cyanogen may be estimated in iodine (1) by ascertaining the difference in titrating with thiosulphate in acid and neutral solutions, (2) by gravimetrically determining the amount of sulphate produced on reducing the cyanogen iodide in neutral solution (compare preceding abstract). The results are not very accurate. A. R. L.

Detection of Cyanogen in Iodine. By C. Meineke (*Zeit. anorg. Chem.*, **2**, 165—167).—Varying amounts of cyanogen iodide were added to saturated aqueous solutions of iodine, so that the total volume was 20 c.c. The mixture was acidified with a drop of dilute hydrochloric acid, and reduced with such a quantity of sodium thiosulphate that a slight yellow coloration was left. On now adding

ferrous sulphate and alkali, a precipitate of Prussian blue is formed. The limit of the test was found to be 1 part of cyanogen in 54,000 parts of water.

When a neutral solution of iodine containing cyanogen iodide and a small quantity of potassium iodide is treated with centinormal thiosulphate until the yellow colour has almost disappeared, and a 0·1 per cent. solution of starch added, the well-known iodide of starch reaction becomes apparent after a while. A more reddish tone is, however, obtained than that produced by solutions of pure iodine. The presence of 0·008 gram of cyanogen iodide in 20 c.c. of water may be detected by the formation of a precipitate of barium sulphate on adding barium chloride to the last-mentioned solution after the addition of thiosulphate (compare preceding abstracts).

A. R. L.

Oxidation of Glycerol in Acid Solution. By S. Salvatori (*Staz. Sper. Agrar.*, **21**, 130—140).—Experiments, suggested by Olivieri and Spica's method for the estimation of glycerol in wine (Abstr., 1891, 369), were made on the oxidation of glycerol by permanganate: a solution containing 0·1062 per cent. of glycerol was employed. To 10 c.c. of this solution, acidified with sulphuric acid, the permanganate was added as long as the colour disappeared, the addition being stopped when the colour produced by 2 or 3 drops was no longer destroyed by continued heating of the solution on a water-bath. The results obtained were rather high. Although the action was much more rapid, similar results were obtained when the solution was actually boiled, instead of heating it on a water-bath, and also when increased amounts of acid were employed. The employment of permanganate in excess gave rise to increased reduction. Finally, when stronger solutions of glycerol were used, the amount of permanganate reduced was found to increase at a still greater rate; thus, whilst 10 c.c. of 0·01 per cent. glycerol reduced 10·5 c.c. of permanganate solution, the same amount of 0·05 per cent. glycerol reduced 67 c.c.

After discussing the various methods employed for the oxidation of glycerol (compare Legler, *Chem. Zeit.*, 1886; Cross and Bevan, *Chem. News*, 1887, 2; and Planchon, *Compt. rend.*, **107**, 246), the author describes the following methods in which he adopted Planchon's reaction (*loc. cit.*):—

The apparatus consists of a small, wide-mouthed flask, furnished with a reflux condenser, the upper end of which is connected with the upper end of a burette; the lower end of the burette is connected by means of india-rubber tubing with a second tube; both these tubes are connected with a large bulb. The burette is surrounded by a second tube, and kept cool by means of cold water. The analysis is carried out as follows:—The necessary amounts of permanganate (20 c.c. of 5 per cent. solution) and sulphuric acid (10 c.c. of 30 per cent. acid) are put into the flask, then a tube containing the glycerol solution (10 c.c.) is carefully put in, so as not to overturn it. The flask is connected with the condenser and immersed in cold water. The measuring apparatus is then filled with mercury and connected with the condenser. The same water is made to pass through the

vessel containing the flask, through the condenser, and through the burette water jacket, so that the temperature is everywhere the same. The flask is taken out of the water-bath, dried, the tube containing the glycerol overturned, and the whole of the contents mixed; the reaction is finished in a minute or two. The whole apparatus is again cooled, and the increase of volume due to the carbonic anhydride formed is read off and reduced to 0° and 760 mm. pressure. A smaller amount of glycerol solution may be employed, but it is best always to keep to the amounts of permanganate and acid already given. The strength of glycerol solution may vary from 0·05 to 2 per cent. In analysing wine or beer, the amount of glycerol should be approximately ascertained before employing this method.

N. H. M.

Estimation of Glycerol in Wine and other Fermented Liquids. By S. Salvatori (*Staz. Sper. Agrar.*, **21**, 141—145).—50 c.c. of red wine is treated with basic lead acetate, the excess of lead precipitated by sodium carbonate, and the filtered liquid evaporated to about 10 c.c. It is then treated with a mixture of quicklime and anhydrous gypsum, powdered, and extracted with alcohol. The alcoholic solution is evaporated to 10 c.c., mixed with ether (15 c.c.), filtered if necessary, and evaporated to a small bulk. Water is then added to the residue, and the mixture boiled to drive off the alcohol, evaporated to about 10 c.c., and distilled in the apparatus used by v. Törring (Abstr., 1889, 735). A little water is subsequently distilled, in order to remove the last traces of glycerol from the neck of the retort. The glycerol in the distillate, made up to 50 c.c., is determined as already described (see preceding abstract).

The same process is employed with dry white wines. With sweet wines and beer, 100 c.c. is used for the analysis; the distillate is made up to 50 c.c.

The chief difficulty in the process is to get the whole of the glycerol in a state of purity; the alcohol is liable to extract compounds of glucoses with lime, which are not precipitated by ether; on the other hand, if the evaporation and precipitation with ether is repeated, there will be a loss of glycerol.

N. H. M.

Metaphosphoric acid as a Precipitant of Proteïds in the Estimation of Sugar in Milk. By G. Denigès (*Bull. Soc. Chim.* [3], **7**, 493—499).—For the optical determination of sugar in milk, 10 c.c. of the sample is mixed with a 5 per cent. solution of sodium metaphosphate (1·5 c.c.), hydrochloric acid (0·3 c.c.), and some water added, and, after well agitating the mixture, it is diluted to 50 c.c., filtered, and the filtrate examined by the polarimeter in a 500 mm. tube. Metaphosphoric acid is stated to exert no influence on the rotatory power of milk sugar.

A. R. L.

New Method for the Estimation of Grape Sugar. By A. W. Gerrard (*Pharm. J. Trans.* [3], **52**, 208—210).—When to a volume of Fehling's solution there is added just sufficient potassium cyanide to discharge the blue colour, and the liquid is mixed with a second

equal volume of Fehling's solution, grape sugar will produce no precipitate in the boiling mixture, but its gradual addition causes a steady disappearance of the blue colour, and at the sharp end change the glucose value will be found approximately equal to half that of ordinary Fehling's solution. The author's explanation is, that the double potassium and copper cyanide formed in the first instance, being a solvent of the cuprous oxide, prevents its precipitation when formed by the action of the glucose on the second volume of the Fehling, in which reduction is presumed to take place as in the ordinary method. In practice, he keeps three solutions in separate bottles, as follows:—(1) Copper sulphate, 69·3 grams, water to 500 c.c. (2) Rochelle salt, cryst., 175 grams; sodium hydroxide, 76·56 grams, water to 500 c.c. (3) Potassium cyanide, 33 grams (or a sufficiency), water to 500 c.c. For testing, 5 c.c. of each solution is mixed with 50 c.c. of water, and to this liquid, boiling in an open vessel, the grape sugar is added until the blue colour disappears. It returns shortly afterwards by absorption of oxygen from the air, but this does not affect the accurate observation of the end reaction. In case any precipitate is formed, the cyanide solution must be strengthened. The author had kept some of this solution for three months without change. In the discussion following the paper, it was suggested that glycerol might advantageously replace the alkaline tartrate. R. R.

Estimation of Starch. By GUICHARD (*Bull. Soc. Chim.* [3], **7**, 554—560).—The following method is recommended by the author for the estimation of starch in cereals. The flour (5 grams ?) is boiled in a reflux apparatus with a saturated solution of oxalic acid (90 c.c.) for a quarter of an hour; the solution now contains soluble starch, dextrin, and a little glucose. Nitric acid (10 c.c.) is then added, and a portion of the filtrate boiled for an hour in a reflux apparatus and polarised. The amount of glucose thus obtained is converted into starch by multiplying by 0·9. The insoluble residue, after washing, is free from starch. The results need none of the corrections that are necessary in other saccharification methods, since only traces of nitrogenous matters are dissolved, and much less cellulose is attacked than by the use of nitric acid alone. When cellulose, in the state of raw material, is boiled with nitric acid for an hour, the liquid reduces Fehling's solution, and is optically active; after repeating the operation several times, however, with fresh quantities of acid, a liquid is finally obtained which exerts no effect on Fehling's solution. The substances saccharified are lignin, incrusting matters, pectin-like substances, gummy matters, and sugars. Vegetable ivory is more readily attacked than any other cellulose in the form of raw material. The residue left undissolved from these operations is not pure cellulose, but contains hydrocellulose, besides a small quantity of nitro-compounds which can be partially removed by washing with alcohol and ether. Hydrocellulose is distinguished from oxycellulose by its incapability of fixing colouring matters, but the two compounds behave similarly towards Fehling's solution. Sulphate of iron gives a rusty precipitate on boiling with hydrocellulose. A. R. L.

Detection of Wheat-flour in Rye-flour. By A. KLEEBERG (*Chem. Zeit.*, **16**, 1072—1073).—The author recommends the following simple method, based on the peculiar behaviour of wheat gluten. A pinch of the suspected flour is put on an object glass, 7·5 cm. long and 2·5 cm. wide, and well mixed with 5 or 6 drops of luke-warm water. It is very important there should be enough water to float the starchy particles, as the experiment will fail if a paste has formed. The mixture is now spread over $\frac{2}{3}$—$\frac{3}{4}$ of the object glass, and a second slide is put over it in such a way that the free end of the one lies at the right, and of the other at the left, side. The slides are now firmly pressed together, wiped dry, and then passed several times over each other. Already, when pressing the plates, whitish superficies make their appearance, and on moving the plates they readily roll out. If much wheat-flour is present, the rods are long and thick, but if there is only a little of it, they are short and thin. With a little practice, the operator will be able to easily detect an admixture of 5 per cent. of wheat-flour. L. DE K.

Estimation of Acetone in Urine. By R. SUPINO (*L'Orosi*, 1892, 217—221).—The action of iodine and caustic alkali on acetone, represented by the equation $CO(CH_3)_2 + 3I_2 + 4NaHO = CHI_3 + CH_3{\cdot}COONa + 3NaI + 3H_2O$, forms the basis of the following method of estimating acetone when present in urine. On distilling the urine, the acetone comes over with the first runnings; potash or soda and a solution of iodine in potassium iodide are then added to this fraction until the brown colour is persistent; the colour is then discharged by soda, and the solution extracted with ether until the aqueous layer loses its turbidity. The ethereal solution is separated, evaporated to dryness, the residual iodoform dissolved in concentrated alcohol and boiled for 20 minutes with caustic soda free from chloride in a reflux apparatus, when the reaction represented by the equation $CHI_3 + 4NaHO = 3NaI + H{\cdot}COONa$ occurs. The alcohol is now evaporated, the aqueous solution acidified with dilute nitric acid, and excess of N/10 silver nitrate solution added; the silver iodide is filtered off, and the excess of silver nitrate determined by titration with standard potassium ferrocyanide solution, using ferric sulphate as an indicator. The method gives good results. W. J. P.

Estimation of Lactic acid in Milk. By W. THÖRNER (*Chem. Zeit.*, **16**, 1469—1470; 1519—1520).—The author again calls attention to a process which he has used since 1887, and which has also been independently worked out by Pfeiffer. 10 c.c. of the sample is diluted to 30 c.c. with distilled water, and mixed with 5 drops of a 5 per cent. alcoholic solution of phenolphthaleïn. Decinormal soda is now added from a delicate burette until the liquid is decidedly reddish. If a milk should take 1 c.c. of the alkali, the author calls this 10° of acidity. If no distilled water is at hand, common water may be used after five minutes boiling to drive off any carbonic anhydride.

Fresh milk usually shows 8—16° of acidity. When the acidity reaches 22°, the milk coagulates on boiling. L. DE K.

Estimation of Oleïc acid. By O. Hehner (*Analyst*, **17**, 181—183).—The author investigated the well-known process based on the separation of lead oleate from the lead salts of fixed fatty acids by means of ether. The oleïc acid obtained by decomposing the ethereal solution by means of hydrochloric acid was in no case pure, as its iodine absorption varied from 58 to 100 per cent., 90 per cent. being its theoretical number. On the other hand, the acids liberated from the insoluble lead salts absorbed a considerable amount of iodine, ranging from 18 to 35 per cent., showing the presence of a considerable amount of oleïc acid. The figures show most conclusively to the author's mind that the method of oleïn determination founded on the relative solubilities of the lead salts in ether is utterly untrustworthy. L. de K.

Estimation of Oleïc acid. By L. de Koningh (*Chem. News*, **65**, 259).—Oleïc acid may be estimated with great accuracy in fats of the ordinary type, by means of the ether method (compare preceding abstract); but, in order to get trustworthy results, it is necessary to decompose the insoluble lead salts by means of hydrochloric acid, and to recrystallise the fatty acids so obtained from hot alcohol. The mother liquor will generally contain a small quantity of oleïc acid, which may be recovered by converting it into a lead salt and extracting this with ether. The author further states that the lead salts of stearic and palmitic acids are absolutely insoluble in cold ether, and sees no sufficient cause to abandon the lead-ether method. L. de K.

Estimation of Cholic acid in Bile. By Lassar-Cohn (*Ber.*, **26**, 146—151).—See this vol., ii, 220.

Estimation of Fat in Milk by Babcock's Method. By A. W. Stokes (*Analyst*, **17**, 127—130).—This process is almost identical with Leffmann and Beam's method (Abstr., 1892, 1532). Milk is mixed with an equal bulk of strong sulphuric acid in a bottle with a graduated neck, and, whilst hot, whirled for eight minutes in a centrifugal apparatus making 500 revolutions per minute. After filling with hot water to the beginning of the neck, they are again whirled for two minutes. More hot water is now added up to the top of the neck; another two minutes whirling is given, and the fat which by this time has collected in the neck is read off without delay.

The results obtained by the author can hardly be called satisfactory, although the process may be recommended as a rough-and-ready method. L. de K.

Babcock's Method of Milk Analysis. By F. T. Shutt (*Analyst*, **17**, 227—229).—The author, who has extensively used this process (see preceding abstract), states that when the Babcock test is made according to the instructions given with the machine, strictly trustworthy results are obtained. His test analyses are certainly satisfactory (also compare Abstr., 1891, 1339). L. de K.

Estimation of Total Solids in Milk. By H. D. Richmond (*Analyst*, **17**, 225—227).—Although the numerous processes now in use are sufficiently accurate for technical purposes, scientifically accurate results cannot be obtained. The author thinks, however, that the following process is a step in the right direction:—3 grams of asbestos, best quality, is ignited in a platinum dish in a muffle, and the whole is weighed. 5 grams of milk is added, and the dish is placed for two hours on the water-bath. After drying for 12 hours in a water-oven at 98°, the author has always succeeded in getting a perfectly constant weight.

The residue serves excellently for the purpose of ash estimation.

L. de K.

Estimation of Butter Fat in Milk. By L. G. Patterson (*Exper. Stat. Record.*, **4**, 267; from *Mississ. Stat. Bul.*, No. 21, 1892).—The method is a modification of Beimling's. The Beimling centrifugal and test bottles are used, and the milk (15 c.c.) is treated with 1·5 c.c. of amyl alcohol (instead of amyl alcohol and hydrochloric acid). The bottles are whirled for a minute, nearly filled with hot water, again whirled for half a minute, and the columns of fat read off. The results obtained by the method were sometimes higher and sometimes lower than those obtained by the original method, the differences averaging 0·03 per cent. The advantages of the new method are: (1) a sharply defined fat column, (2) the absence of charring of the fat, (3) the contents of the bottles never foam over, (4) quickness, (5) cheapness.

N. H. M.

Volumetric Estimation of Alkaloïds. By A. H. Allen (*Chem. News*, **66**, 259).—The author points out that the neutrality of phenolphthaleïn towards, and its application in the estimation of, many alkaloïds (compare Barthe, this vol., ii, 146) was mentioned by him and commonly known in 1891. When applied in the method of analysis of a mixture of cinchona alkaloïds, in which the cinchonidine is precipitated by a neutral solution of sodium potassium tartrate, the precipitate is washed once with a saturated solution of the precipitant, instead of with water as is usually done, is then immersed in boiling water and titrated with N/20 alkali, using phenolphthaleïn as indicator, and inasmuch as the latter is neutral to Rochelle salt, whilst the cinchonidine tartrate acts towards it like free tartaric acid, the alkaloïd may in this way be readily estimated. Quinidine hydriodide can be estimated in a similar manner. Methyl-orange, owing to its neutrality towards alkaloïds and organic bases, may be used as an indicator for the titration of these substances, urea, caffeïne, theobromine, and perhaps aniline excepted. The ethereal solution of the alkaloïd is placed in a stoppered cylinder with aqueous methyl-orange, and titrated with N/50 hydrochloric acid.

D. A. L.

General and Physical Chemistry.

Separation and Striation of Rarefied Gases under the Influence of the Electric Discharge. By E. C. C. Baly (*Phil. Mag.* [5], **35**, 200—204).—On passing an electric discharge through a vacuum tube containing a small quantity of hydrogen, the hydrogen lines are only observed in the spectrum of the negative glow, and not at all in the body of the tube. This the author shows to be due to accumulation of the hydrogen round the negative pole; by employing conveniently shaped tubes containing mixtures of carbonic anhydride and hydrogen at about $\frac{3}{4}$ mm. pressure, so complete a separation of the hydrogen ensues that, on sealing off the portion of the tube containing the positive pole, it is found to show only a trace of hydrogen by spectroscopic tests. Mixtures of hydrogen with other gases, such as nitrogen, carbonic oxide, sulphurous anhydride, iodine, or mercury vapour, behave in a precisely similar manner to the above. In a tube containing carbonic oxide and carbonic anhydride, the former gas separates at the negative pole, whilst with a mixture of carbonic anhydride and nitrogen, very complete separation of the carbonic anhydride occurs; sulphurous anhydride is separated from a mixture of that gas with carbonic anhydride. Air has to be highly rarefied before separation occurs, and then the oxygen seems to go to the negative pole; no relation could be established between the separation of the various gaseous mixtures and the molecular weights of their constituents.

There seems to be some connection between this kind of separation and striated discharges; strongly marked striæ are only observed when separation occurs, and not if the contents of the tube remain homogeneous. If the formation of a glow round the negative pole be prevented by making the latter a mere point, no striation or separation is observed. Pure gases do not stratify, iodine, sulphur, arsenic, and mercuric iodide giving only a phosphorescence throughout the tube. Hydrogen, prepared in a state of considerable purity, showed but traces of striation. The author concludes that pure hydrogen would not stratify at all, and that striation generally is due to the separation of two gases. W. J. P.

Atomic Refractions of the Elements with respect to Sodium Light. By F. Zecchini (*Gazzetta*, **22**, ii, 592—604).—The increasing application of Pulfrich's total refractometer to the determination of refraction constants renders a knowledge of the atomic refractions of the elements with respect to the D ray of great importance. The author has therefore calculated these constants from a large number of measurements made on organic compounds by several observers, and has tabulated the results in the present paper. The following table contains the values thus arrived at:—

	$\frac{n_D - 1}{d}$.		$\frac{n_D - 1}{d}$.
Carbon	4·71	Bromine	15·34
Hydrogen	1·47	Iodine	25·01
Alcoholic oxygen..	2·65	Increase for each double bond.....	2·64
Aldehydic „ ..	3·33		
Chlorine.....	10·05		

W. J. P.

Molecular Refraction and Dispersion. By J. H. GLADSTONE (*Phil. Mag.* [5], **35**, 204—210).—The author has measured the refraction constants of ferropentacarbonyl (compare Abstr., 1891, 1322), and considers that his results favour Mond's suggestion that this substance is a ring compound having the constitution

$$Fe<\begin{matrix}CO\cdot CO\\CO\cdot CO\end{matrix}>CO.$$

The molecular refraction for the α hydrogen line is about 68·5, and the molecular dispersion between the γ and α hydrogen lines is 6·6; the molecular dispersion of each carbonyl group is 1·3, the value shown by this group in nickel tetracarbonyl (compare Armstrong, Proc., 1893, 57).

The author has calculated the atomic refractions of indium and gallium from the later observations of Soret on the alums of these metals (*Arch. Sci. Phys. Nat., Genève*, **14**, 96). For indium, $R_A = 13·7$, and for gallium, $R_A = 11·6$.

Calculations of the atomic refraction of sulphur from observations made on the element in the three states, and on its simple compounds with carbon and the halogens, give very similar results; the values are lower than those deduced from measurements made on certain organic sulphur compounds by Nasini and Costa (Abstr., 1891, 1305; 1892, 34).

The refraction equivalents of liquid oxygen and ethylene, as determined by Liveing and Dewar (this vol., ii, 201), agree well with the theoretical numbers; the refractive indices of liquid nitrous oxide seem to indicate that the nitrogen in this substance is in the same condition as in the nitriles (compare Armstrong, *loc. cit.*).

W. J. P.

Spectrochemistry of Nitrogen. By J. W. BRÜHL (*Ber.*, **26**, 806—809).—By subtracting from the molecular refraction of a nitrogenous compound the sum of the atomic refractions of the atoms other than nitrogen contained in it, these atomic refractions being assumed to be the same as those they have in the free state, the atomic refraction of the nitrogen atom itself is calculated. This for yellow light is found to be: singly bound (in ammonia), 2·50; doubly (in nitrous oxide), 2·27 at least; triply, or fivefold ? (in free nitrogen), 2·21. The values do not continuously increase, as in the case of carbon; hence it is argued that "single, double, and triple linking of carbon atoms is something quite different in its nature from single, double, and triple linking of nitrogen atoms." Compounds containing the group C:N have a molecular refraction greater than that cal-

culated, and the same is true for cyanogen, which contains the group C:N. But, strangely enough, hydrogen cyanide has a molecular refraction about equal to the calculated value; hence this gas cannot contain the group C:N, and "cyanogen and hydrogen cyanide cannot have a similar constitution." C. F. B.

Influence of Temperature on the Rotatory Power of Liquids. By A. Colson (*Compt. rend.*, **116**, 319—322).—A continuation of the discussion with Friedel. When aniline is dissolved in diacetyltartaric acid or its anhydride, the solution is lævogyrate, whereas it might have been expected that it would be dextrogyrate, since C_6H_5N is heavier than $C_2H_3O_2$. It is, of course, possible that molecular combinations are formed with the excess of aniline, but any objection on this ground would be equally fatal to all the evidence obtained from solutions in alcohol or benzene.

The rotatory power of isobutylic isoamylic oxide changes sign at a very low temperature, and the results obtained with this and two similar liquids are given in the following table, and it will be observed that as the temperature rises, diisoamylic oxide shows a maximum of rotatory power, and methylic amylic oxide passes through a minimum:—

Temperature ..	−40°.	−21°.	−4°.	+15°.	+40°.	+100°.
Isobutylic isoamylic oxide	−0° 6′	+0° 4′	+0° 11′	+0° 13′	+0° 15′	—
Diisoamylic oxide	?	+0 21	+0 35	+0 42	+1 3	+1° 16′
Methylic isoamylic oxide	+1° 4′	+0 10	+0 12	+0 20	+0 28	—

It would seem that chemical constitution is not necessarily the preponderating factor in determining either the sign or the value of the rotatory power, but physical causes may produce considerable variations in the optical activity of certain liquids. C. H. B.

Stereochemistry. By C. Friedel (*Compt. rend.*, **116**, 351—353).—A continuation of the discussion with Colson. C. H. B.

Alteration of the Sign of Optical Rotation. By J. A. Le Bel (*Bull. Soc. Chim.* [3], **7**, 613—649).—A polemical paper.

Electrochemical Investigations. By F. Exner (*Monatsh.*, **13**, 851—871).—The author has determined the potential differences between metals and bases, making use of the method employed for the like determination in the case of the acids. The metals all become negatively charged, and the solutions positively. The potential differences are of the same order of magnitude as those observed for solutions of acids and salts. The values increase with potash and soda very considerably, with rise in concentration with all metals, except magnesium, the values for which are nearly all lower than those obtained in pure water. The occurrence of a maximum at a certain concentration, so frequently noticed in the case of the acids, was not observed with the bases, except in the two cases of mercury

and tin in ammonia solutions. With the acids, the potential differences were found to vary periodically with the atomic weights of the metals, so that certain metals always gave maximum and minimum values; a like behaviour is to be observed in the case of the bases.

With the aid of the numbers obtained for the potential differences between metals and acids and metals and bases, the author has been further able to determine potential differences between acids and bases. It is found that bases in contact with acids become negatively charged, and that acids therefore behave towards bases as they do towards the metals. Only one exception was noticed, in the case of acetic acid and ammonia, where the acid in very concentrated solution becomes feebly negative. Concentration exercises a very marked influence in all cases, a constant increase in the potential differences with increase of concentration being observed for hydrochloric, hydrofluoric, and acetic acids. Increase to a maximum with subsequent decrease was noticed for sulphuric, nitric, hydrobromic, and oxalic acids. H. C.

Electrometric Study of Potassium Hydrogen Triplatohexanitrite. By M. Vèzes (*Compt. rend.*, **116**, 185—188).—The author has measured the electrical conductivity of dilute solutions of potassium hydrogen triplatohexanitrite, $Pt_2O(NO_2)_6K_2H_4 + 3H_2O$, mixed with various proportions of potassium hydroxide (compare this vol., ii, 213). The normal salt corresponds with the mixture, $Pt_2O(NO_2)_6K_2H_4 + 4KOH$, but as the dilution increases it is stable only in presence of a greater and greater proportion of alkali. In the dilute solutions, several days are required before the liquid attains a condition of equilibrium, and the time required increases with the degree of dilution. C. H. B.

Relation of Volta Electromotive Force to Pressure. By G. Gore (*Phil. Mag.*, [5], **35**, 97—112).—A vertical glass tube, some 3 metres long, is filled with an electrolyte and closed by two similar electrodes, by means of which circuit with a galvanometer is completed; on allowing the tube to remain undisturbed until all sign of current, or variation of current, ceases and then reversing the two ends of the tube, sufficient potential difference is set up to cause considerable deflection of a Thomson's reflecting galvanometer. A large number of different metallic electrodes and of electrolytes, such as solutions of salts and acids, were employed, and in nearly every case an appreciable current was developed; the E.M.F. established is about 0·005 volt. The deflection of the galvanometer does not attain a maximum for some 5—10 minutes after reversing the position of the tube; this maximum deflection when once established diminishes very slowly, and, in a test case, had only decreased by one-third after 16 hours. A concentrated electrolyte is more active than a dilute one.

A number of experiments were made showing conclusively that the development of the current is due solely to the pressure of the column of electrolyte; the author finally discusses his results in their

relation to the work of Gibault on the change of E.M.F. accompanying increase of pressure in various cells (*Compt. rend.*, **113**, 465).

W. J. P.

Behaviour of Electrolytes in Mixed Solvents. By A. J. WAKEMAN (*Zeit. physikal. Chem.*, **11**, 49—74).—The author has found the following numbers for the relative speeds of the ions in aqueo-alcoholic solutions:—

Percentage of alcohol.	H.	K.	Na.	Cl.
50	101·8	23·9	20·1	24·7
40	128·1	27·6	21·9	28·4
30	156·4	32·4	24·6	33·6
20	197·3	39·3	29·1	40·7
10	242·7	49·7	36·7	51·3
0	320·5	67·9	45·5	73·5

The electrical conductivities of a number of organic acids in such solutions were determined, and from the results obtained it appears that Ostwald's formula $\frac{m^2}{(1-m)v} = k$, which is very accurate when the acids are dissolved in water, is not in this case valid. Acetone influences the dissociation of a substance in water in the same way as alcohol does, but in a greater degree.

Experiments were also made on the effect of alcohol in reducing the rate of inversion of sugar solutions by acids. There is no definite relation between the influence on the molecular conductivity and on the reaction velocity. It is possible that this difference is due to the change in the viscosity of the liquid occasioned by the addition of the alcohol.

Numerous tables and curves of the results are given by the author.

J. W.

The Temperature of Explosion. By A. MITSCHERLICH (*Ber.*, **26**, 399—403; compare this Journal, 1877, i, 42; this vol., ii, 202).—The temperature of explosion of a mixture of hydrogen and oxygen in the proportion of 2 : 1 by volume is found to vary with the pressure and with the shape of the containing vessel. For one and the same vessel, however, and for pressures less than 760 mm., the temperature of explosion falls as the pressure of the gaseous mixture is diminished, and the fall in temperature is proportional to the diminution of pressure. With pressures higher than 760 mm., great experimental difficulties are encountered, and the only certain conclusion that can be drawn from the experiments is that the temperature of explosion of gases is higher when they are compressed than when they are uncompressed. This is directly contrary to hitherto accepted views.

C. F. B.

Ignition Temperature of Explosive Gaseous Mixtures. By F. FREYER and V. MEYER (*Zeit. physikal. Chem.*, **11**, 28—37; compare Abstr., 1892, 680).—The authors have studied the temperatures at which various explosive gaseous mixtures ignite, using for low

temperatures an oil-bath, and for higher temperatures boiling sulphur (448°), phosphorus sulphide (518°), stannous chloride (606°), zinc bromide (650°), and zinc chloride (730°). The mixtures were either led through a tube immersed in the bath, or were enclosed in bulbs which were suddenly plunged into the hot liquid or vapour. The following results were obtained. The mixture did not explode at the lower temperature in each column, but did so at the higher.

Equivalent mixtures.	Free current.	Closed bulbs.
Hydrogen, oxygen.....	650—730°	530—606°
Methane, oxygen	650—730	606—650
Ethane, oxygen	606—650	530—606
Ethylene, oxygen	606—650	530—606
Carbon monoxide, oxygen ...	650—730	650—730
Hydrogen sulphide, oxygen..	315—320	250—270
Hydrogen, chlorine.....	430—440	240—270

It appears from these experiments that ignition always takes place at a lower temperature when the mixture is in a closed vessel than when passing freely through an open tube. If, however, an open vessel containing the gas is heated suddenly, the explosion takes place at the lower temperature. The speed of the current was so small that the difference cannot be explained by the gases being insufficiently heated. J. W.

Temperatures of Explosion of Gaseous Mixtures. By V. Meyer (*Ber.*, **26**, 428—429).—The temperature of explosion of a mixture of hydrogen and chlorine has already been shown by the author and Freyer (preceding abstract) to be very irregular. When bulbs, filled with this mixture, are dipped suddenly in the dark into boiling dimethylaniline (b. p. 193°), explosion generally occurs, but not always; whereas by employing boiling aniline (b. p. 182°) the mixture only exploded in two out of 40 experiments. Small quantities of admixed foreign gases, as well as the nature of the vessel enclosing the mixture, are of considerable influence. A. R. L.

Specific Heat of Liquid Ammonia. By C. Ludeking and J. E. Starr (*Amer. J. Sci.* [3], **45**, 200—202).—The specific heat of liquid ammonia was directly determined, about 10 grams of the liquid being enclosed in a steel cylinder weighing nearly 71 grams, the whole heated to the boiling point of carbon bisulphide, and then dropped into a brass calorimeter whose water value was 1·36 cal.; it contained 150 grams of water at about 25°. Experiments were also made in which the cylinder and contents were first cooled in melting ice, and then introduced into the warm calorimeter water. Three determinations were made by each of the above methods, the average value for the specific heat of liquid ammonia obtained from the whole series being 0·8857. H. C.

Specific Heats of Erythritol and Mannitol. By W. Louguinine (*Ann. Chim. Phys.* [6], **27**, 138—144).—The author has made certain improvements in the apparatus previously described (*Ann. Chim.*

Phys. [5], **27**, 398), and has now employed it in determining the specific heats of erythritol and mannitol respectively. The specific heat of erythritol was found to be 0·3520 as the average of three experiments, in which the maximum difference amounted to 0·54 per cent.; that of mannitol proved to be 0·3277 as the average of five experiments with a maximum difference of 1·13 per cent., or, neglecting one obviously incorrect result, 0·3287 as the average result of four experiments with a maximum difference of 0·3 per cent. The determinations were made between 100° and 20°. F. S. K.

Heat of Formation of Aragonite. By H. Le Chatelier (*Compt. rend.*, **116**, 390—392).—The heat of formation of aragonite and calcite was determined by dissolving the minerals in hydrochloric acid. The values obtained for the heat of combination, CaO sol. + CO_2 gas = $CaCO_3$ sol., were, with Iceland spar +21·03 Cal., white, opaque calcite +20·96 Cal., fibrous aragonite +21·26 Cal., and crystallised aragonite +21·33 Cal. The mean value for the heat of conversion of aragonite into calcite is −0·3 Cal., instead of the value +2 Cal., adopted hitherto.

Since aragonite has a higher specific gravity and a higher heat of formation than calcite, its zone of stability should necessarily correspond, as in the case of quartz and the diamond, with lower temperatures and higher pressures than those which correspond with their reversible transformation. C. H. B.

Heat of Dissociation of some Acids. By E. Petersen (*Zeit. physikal. Chem.*, **11**, 174—184).—The author points out that the heat of dissociation of an acid may be calculated from the heat of dilution, as the latter should be equal to the change in the amount of dissociation on dilution multiplied by the heat of dissociation. A comparison between the heats of dilution of a number of acids, calculated by the above method and directly determined, shows that, allowing for the necessarily large errors of experiment, there is a general agreement between the two. The heat of dissociation may also be calculated from the heat developed in the action of acids on their sodium salts. According to Arrhenius' theory of isohydric solutions, a change in the amount of the dissociation of the acid takes place in this case, which may be calculated by the law of mass action. This change, multiplied by the heat of dissociation of the acid, should be equal to the heat developed on mixing the acid and its sodium salt. In most cases, the heat evolved is too small for direct determination, but the author has been able to verify the theory in two cases, those of hydrogen and sodium fluoride, and of phosphoric acid and sodium dihydrogen phosphate. The observed and calculated values are in fair agreement. H. C.

Behaviour of Colloïds in Organic Solvents (Organosols) at the Critical Temperature of the Solvent. By E. A. Schneider (*Zeit. anorg. Chem.*, **3**, 78—79).—A colloïdal solution of silver in ethyl alcohol (organosol, Ag[EtOH]), was prepared by dialysing the purified hydrosol into absolute alcohol. It was then heated in sealed

tubes to 250—255° (in the vapour of boiling amylic benzoate), that is, 20° above the critical temperature of ethyl alcohol. The silver coagulated to a reddish-brown mass, and did not redissolve when the alcohol was cooled. C. F. B.

Graphical Deductions from the Solution Isotherms of a Double Salt and its Components. By F. A. H. Schreinemakers (*Zeit. physikal. Chem.*, **11**, 75—109).—The author (*Zeit. physikal. Chem.*, **9**, 57) has given a graphic method for representing the behaviour of a system consisting of three substances, and in this paper describes how it may be applied to the case of a double salt and its two components, showing how the system behaves for variations of temperature, and of the proportion of the substances present. J. W.

Applications of Beckmann's Boiling Point Apparatus. By M. Roloff (*Zeit. physikal. Chem.*, **11**, 7—27).—By means of Beckmann's apparatus, the author has made a series of determinations of the boiling points of aqueous solutions of potassium chloride, varying in concentration from 0·5 to 18·5 grams of salt in 100 grams of water. His results agree fairly well with those formerly obtained by Tammann and Dieterici. He gives a table showing the relation between the elevation of the boiling point of aqueous solutions and their osmotic pressure. Solutions of volatile substances (acetic, formic, nitric, and hydrochloric acids) were also investigated, with results in accordance with the theory as developed by Nernst (*Zeit. physikal. Chem.*, **8**, 110). Nernst has shown theoretically (*Zeit. physikal. Chem.*, **11**, 1) that the reciprocal of the molecular elevation of the boiling point of a homogeneous mixed solvent is composed, according to the simple mixing formula, of the reciprocals of the molecular elevations of the two components and the percentage composition of the mixture. From solutions of naphthalene in a mixture of benzene and chloroform, and of boric acid in mixtures of water and acetic acid, the author obtained numbers in confirmation of this theoretical deduction. Solutions of potassium chloride in water and acetic acid showed that the elevation is nearly independent of the quantity of acetic acid present (in which the salt is insoluble).

An arrangement is described and figured by means of which boiling point determinations may be made at any desired constant pressure. J. W.

Measurements of Van der Waals' Surface for Mixtures of Carbonic Anhydride and Methylic Chloride. By J. P. Kuenen (*Zeit. physikal. Chem.*, **11**, 38—48).—The author has investigated various mixtures of carbonic anhydride and methylic chloride with respect to their pressure, volume, and temperature, in order to test the validity of Van der Waals' theory (*Zeit. physikal. Chem.*, **5**, 133) as applied to mixtures. He employed a Ducretet compression apparatus, and found it necessary to use a small piece of iron rod, set in motion within the experimental tube by means of an electromagnet, in order to hasten the attainment of equilibrium. Van der Waals' theoretical deductions were in general confirmed. There exists for each mixture

a temperature, called by the author the critical contact point, which corresponds with the critical point of a pure substance. The phenomenon of retrograde condensation was observed; that is, for a mixture, the quantity of liquid at first increases on compression, then reaches a maximum, and finally diminishes to the vanishing point. At the temperatures and pressures of experiment, no indication of the coexistence of three phases was observed. J. W.

Determination of the Molecular Weight from the Rate of Evaporation. By H. KRONBERG (*Monatsh.*, **14**, 24—27).—If a non-volatile substance is dissolved in a fairly volatile liquid, the rate of evaporation of the latter is decreased. This may be considered as due to the fact that, with the solution, the surface exposed consists partly of the volatile molecules of the solvent and partly of the non-volatile molecules of the dissolved substance, and not, as when the solvent alone is exposed, solely of volatile molecules. The greater the number of non-volatile molecules the less the evaporation, or, in other words, the rate of evaporation of such a solution as the above will decrease regularly with the concentration, and will be inversely proportional to the molecular weight of the dissolved substance. The molecular weight of any compound might, therefore, be determined from the rate of evaporation of one of its solutions, just as from the reduction of the freezing point.

To carry out a determination, weighed quantities of two solutions, one of a substance of known, and the other of the substance of unknown, molecular weight, in the same solvent, should be exposed either in the open air or in a vacuum for some length of time, and then reweighed. The losses in each case, calculated for 100 parts of the pure solvent, will be inversely proportional to the molecular weights of the dissolved substances, and since one of these is known, the other can then be ascertained. H. C.

A more Exact Cryoscopic Method. By E. H. LOOMIS (*Ber.*, **26**, 797—801).—The apparatus consists of two thin-walled test-tubes placed one within the other, and joined at the upper ends by a piece of india-rubber tubing, the annular space between them being about 1 mm. in thickness. The inner test-tube measures 28 × 3 cm., and its bottom is drawn in to prevent the formation of compact pieces of ice upon it; an india-rubber ring placed round it prevents it from touching the outer test-tube. Through its cork passes a thermometer, the scale-divisions (0·01°) of which are 0·4 mm. long, and a stirrer, consisting of a glass rod with a platinum ring; to the outer side of which a bit of a feather is so attached as to sweep the walls of the test-tube and prevent the formation of ice upon them. The temperature is read to 0·0001 with a microscope and eye-piece micrometer, 10 of whose divisions are equivalent to 1 of the thermometer's; during the reading, the thermometer is continually tapped by a small electric hammer. Three baths are used: a "main bath," consisting of a copper cylinder, 35 × 6 cm., thickly surrounded with felt, and containing a freezing mixture at 0·3° below the melting point to be determined; a "freezing bath" at −10°; and a "melting bath" at

0°. The process is as follows:—Some ice is formed in the apparatus, and the latter is then brought into the melting bath until the ice has nearly disappeared. It is now placed in the freezing bath; the temperature falls to 0·1—0·2° below the freezing point of the mixture, and the water then begins to freeze. The apparatus is immediately transferred to the main bath, the hammer set in motion, and the temperature read after the lapse of two minutes. It is then again brought into the melting bath until the ice has nearly disappeared, and the process repeated 6—10 times as above; successive readings rarely differ by 0·001°. Solutions of the following substances were examined; the numbers represent the extreme values of the molecular depression (lowering of freezing point ÷ gram-molecules per litre), the corresponding number of gram-molecules per litre being 0·01—0·20; except in the case of alcohol, where it was 0·01—0·16; sodium chloride, 3·67—3·44°; cane sugar, 1·71—1·96°; magnesium sulphate, 2·65—2·08°; alcohol; 1·72—1·83°; sulphuric acid, 4·49—3·85°; phosphoric acid, 2·31—1·79°, carbamide, 1·72—1·83°. The rise or fall of the molecular depression with increasing concentration is, in all the cases examined, a continuous one. C. F. B.

Freezing Points of Sulphuric acid of Different Concentrations, and the Sulphuric acid contained in the Solid and Liquid Portions. By J. THILO (*Chem. Zeit.*, **16**, 1688—1689).—The author has determined the freezing points of sulphuric acid of different concentrations and gives his results in the following table.

Formula.	Per cent. H_2SO_4.	Sp. gr.	Freezing point.
H_2SO_4	100·0	1·842	+10·5°
	95·2	1·834	−24·5
	89·17	1·815	−47·0
	88·88	1·813	−55·0
H_2SO_4,H_2O	84·48	1·777	+ 3·5
	83·82	1·772	+ 4·5
	83·74	1·771	+ 5·0
	83·00	1·765	+ 8·0
	80·84	1·743	+ 2·5
	80·09	1·734	+ 1·5
	77·2	1·701	−14·0
	74·85	1·673	−41·0
$H_2SO_4,2H_2O$	73·08	1·650	−70·0
$H_2SO_4,4H_2O$	57·65	1·476	−40·0
$H_2SO_4,6H_2O$	47·57	1·376	−50·0
$H_2SO_4,8H_2O$	40·50	1·311	−65·0
$H_2SO_4,10H_2O$	35·25	1·268	−88·0
$H_2SO_4,11H_2O$	33·11	1·249	−75·0
$H_2SO_4,12H_2O$	31·21	1·233	−55·0
$H_2SO_4,13H_2O$	29·52	1·219	−45·0
$H_2SO_4,14H_2O$	28·0	1·207	−40·0
$H_2SO_4,15H_2O$	26·63	1·196	−34·0
$H_2SO_4,16H_2O$	25·39	1·187	−26·5
$H_2SO_4,18H_2O$	23·22	1·170	−19·0
$H_2SO_4,20H_2O$	21·40	1·157	−17·0
$H_2SO_4,25H_2O$	17·88	1·129	− 8·5

Formula.	Per cent. H_2SO_4.	Sp. gr.	Freezing point.
$H_2SO_4,30H_2O$	15·36	1·109	− 6·5°
$H_2SO_4,40H_2O$	11·98	1·084	− 4·5
$H_2SO_4,50H_2O$	9·82	1·067	− 3·5
$H_2SO_4,75H_2O$	6·77	1·045	0·0
$H_2SO_4,100H_2O$	5·16	1·032	+ 2·5
$H_2SO_4,150H_2O$	3·5	1·020	+ 3·0
$H_2SO_4,200H_2O$	2·65	1·013	+ 4·0
$H_2SO_4,300H_2O$	1·78	1·007	+ 4·5
$H_2SO_4,320H_2O$	1·67	1·006	+ 3·5
$H_2SO_4,340H_2O$	1·58	1·006	+ 2·5
$H_2SO_4,360H_2O$	1·50	1·005	+ 1·5
$H_2SO_4,400H_2O$	1·34	1·005	+ 1·0
$H_2SO_4,1000H_2O$	0·54	1·001	− 0·5

These results give a very irregular curve, crossing the line of zero temperature in five different places.

In most cases, the frozen portion of the acid was separated from that which still remained liquid, and each separately analysed. The percentage of sulphuric acid in the two portions was seldom found to be the same, and only generally where the freezing point curve attains a maximum or a minimum. In other cases the liquid portion contained the larger quantity of sulphuric acid. H. C.

Note by Abstractor.—In the above paper, the author makes no reference to previous determinations. The majority of his results differ considerably from those of Pickering (Trans., 1890, 331), and the assigned *rise* in the freezing point of water on the addition of 1—6 per cent. H_2SO_4, which is out of keeping with the general cryoscopic behaviour of aqueous solutions, must be regarded as very doubtful. H. C.

Freezing Point of very Dilute Solutions. By H. C. Jones (*Zeit. physikal. Chem.*, **11**, 110—116, and *Ber.*, **26**, 547—553).—By using a large quantity of solution (1 litre), a thermometer divided into thousandths of a degree, and having the experimental vessel surrounded by a jacket of stagnant air, the author has succeeded in obtaining numbers for the lowering of the freezing point in very dilute aqueous solutions differing at most by 0·0004°. The correction for the increase in the concentration of the solution, due to the separation of ice, was in all cases applied. The substances investigated were sodium, potassium, and ammonium chlorides. All these salts give continuous curves (almost straight lines) for the lowering of the freezing point, without any of the breaks observed by Pickering.

The following table gives the percentage difference between the results of the two observers for solutions of sodium chloride.

Gram-molecules per litre.	Difference.
0·01	4·0 per cent.
0·005	10·7 „
0·002	11·4 „
0·001	53·8 „

J. W.

Mixtures of Ether and Water. By L. Marchis (*Compt. rend.*, **116**, 388—390).—The author shows that the vapour tension of a mixture of ether and water is independent of the composition of the mixture, and equal to that of anhydrous ether, whether the water added is so small in quantity that it all dissolves in the ether or so large that the solution separates into two layers. H. C.

Determination of the Specific Gravity of Liquids for Practical Purposes. By C. R. A. Wright (*J. Soc. Chem. Ind.*, **11**, 297—305).—The author discusses in detail the appliances ordinarily used for determining the sp. gr. of a given liquid; in cases in which a high degree of accuracy is requisite, he has found certain modifications of the existing instruments of considerable practical use. He describes a modified form of pyknometer which he has found very serviceable, not only in obtaining values exact to five places of figures if requisite, but also in obtaining a series of valuations at different temperatures with comparatively little trouble. Various useful tables for correction are also given. D. B.

Specific Gravity Apparatus. By H. B. Fulton (*J. Soc. Chem. Ind.*, **11**, 305—306).—The apparatus consists of a glass tube, having as uniform a diameter as possible, graduated from zero upwards and weighted with mercury so as to maintain a vertical position when floated in water. The neck by which the mercury bulb is attached is comparatively a long one, so that the centre of gravity may be as low as possible. The lower part of the tube is blown so as to have a small, flattened, protruding bulb to act as a fender and thus insure more accurate readings by preventing the tube from clinging to the sides of the test jar. Water is first poured into the tube to fill it at least to zero on the scale; a little more does not matter, and there should be sufficient to completely cover the sample under examination. Supposing it to have been filled exactly to zero, the tube is then floated in a jar of water and the level at which it floats is read off. This may be, say, 20. The sample is now dropped into the tube, which at once sinks, say, to 55, and the weight of the sample is thus ascertained as $55 - 20 = 35$. At the same time, however, the volume is obtained by noting the displacement of the water inside the tube, and again assuming this reading to be 5, we have at once sp. gr. $= 35/5 = 7$. D. B.

The Molecular Volumes of Dissolved Alkali Salts and their Relation to the Atomic Volumes of the Elements. By J. Traube (*Zeit. anorg. Chem.*, **3**, 11—33; compare Abstr., 1892, 1383).—A not very coherent paper, containing calculations of the molecular volumes of a large number of alkali salts in aqueous solutions of varying concentration, together with a somewhat desultory discussion of the results obtained. The coefficient of electrolytic dissociation is known to increase with dilution of the solution; the molecular volume, on the other hand, decreases, but apparently also tends to a fixed limit. A further relation between the two appears from the fact that, when compounds are compared by pairs—either those of

a base with two different acids, or those of an acid with two different bases—in solutions of varying concentration, the difference between the molecular volumes, at any given concentration, of the two members of a pair remains constant as the concentration varies, if the ratio of the coefficients of electrolytic dissociation of these substances also remains constant; in the opposite case, it also varies. Further, in many cases the difference in molecular volume between the salts of one and the same base with two similarly constituted acids varies considerably with the base. Yet another point is, that salts which are anhydrous, or which do not crystallise with more than $3H_2O$, have, in concentrated solutions, nearly the same molecular volume as in the solid state; this is not the case with salts that crystallise with more than $3H_2O$, but the difference vanishes, or is much reduced, if the salt in solution is regarded as still combined with its water of crystallisation. The fact that this water of crystallisation occupies a less volume than in the free state is accounted for by supposing free water to consist of complex molecules, and the transformation of this water into water of crystallisation to be accompanied by a breaking up of these complex molecules, and a consequent decrease of molecular volume. Finally, the following proposition is enunciated:—The atomic volumes of hydrogen, lithium, and sodium are equal, that of rubidium is nearly equal to that of ammonium, and the atomic volume increases from Na : K : Rb : Cs by a difference which is apparently nearly constant, and has a mean value of 10 units of molecular volume. C. F. B.

Dissociation of Salts into their Ions by Water of Crystallisation. By C. E. Linebarger (*Amer. Chem. J.*, **14**, 604—606).—In the case of a solution of copper sulphate which contains Cu ions, SO_4 ions, and undissociated $CuSO_4$ molecules, the colour must be due to the copper ions, for the SO_4 ions are colourless, and so is the anhydrous molecule of copper sulphate. The colour of the salt crystallised with water of crystallisation must, then, also be due to the presence of free copper ions, or, in other words, *water of crystallisation has the power of dissociating crystallised salts into their ions.* By analogy, this will be true also in the case of colourless salts. C. F. B.

Deviations from the Gaseous Laws in Solutions. By S. J. Thugutt (*Ber.*, **26**, 583—589).—Deviations from the gaseous laws in aqueous solutions may be explained, according to the author, by assuming that hydrolytic, as well as electrolytic, dissociation takes place in the dilute solutions, and that the formation of hydrates occurs in concentrated solutions. H. C.

Diffusion in Aqueous Salt Solutions. By R. Abegg (*Zeit. physikal. Chem.*, **11**, 248—264).—The diffusion experiments described in this paper were carried out with apparatus similar to that used by Arrhenius in his investigations on diffusion in salt solutions (Abstr., 1892, 1265). The diffusing substance was in the first case ammonia, and in the second acetic acid, alcohol being also used in later determinations. All solutions were of normal concentration. The diffu-

sion coefficients were divided by that for water alone, the relative rates of diffusion of ammonia and acetic acid in various salt solutions being in this way referred to those of pure water. The values obtained for ammonia were found generally to be in the order of the fluidities of the salt solutions, but this was not the case with acetic acid. This was found to be due to the fact that acetic acid in most cases alters the osmotic pressure of the salt solution into which it diffuses, and, therefore, the diffusion does not pursue a regular course. Where this alteration in osmotic pressure does not occur, it may be generally stated that the fluidity of water is altered in the same manner, although to a greater degree, by the addition of a salt, as is its resistance to the passage of diffusing molecules. H. C.

Explanation of Affinity. By H. Sachse (*Zeit. physikal. Chem.*, **11**, 185—219).—The author endeavours to deduce a number of the chemical properties of the elements and their compounds from the hypotheses that atoms possess polarity, and that the general mass attraction may become a repulsion if the distance between the centres of gravity is smaller than a certain value. H. C.

The Decomposition of Silver Chloracetate. By J. H. Kastle (*Amer. Chem. J.*, **14**, 586—597).—This was at first studied by placing 0·2015 gram of the salt in a sealed tube with 500 times the amount of water necessary for its complete decomposition, heating the tube in a bath kept at a temperature of 134—135°, removing it, allowing it to cool for 10 minutes, opening it, and determining the amount of undecomposed silver salt by titration with ammonium thiocyanate. The products of decomposition are, of course, silver chloride and glycollic acid. The rate of decomposition was found to rise rapidly until it reached a maximum at the end of 13 minutes, after which it decreased, rapidly at first, afterwards more slowly; at the end of two hours, the decomposition was practically complete. The initial rise was evidently due to the fact of a rise in temperature, for the tube did not acquire the temperature of the bath until after the lapse of 20 minutes. But why should there be a subsequent *fall* in the rate of decomposition, setting in even before the tube had attained its maximum temperature? Special experiments showed that the silver chloride formed had no, and the glycollic acid but little, retarding effect; it was found, however, that the amount of decomposition in the same time is very much less as the amount of water, relatively to that of the silver chloracetate, is greater. The explanation of the decrease in rate of decomposition in the original series of experiments is, therefore, that as the decomposition of the silver chloracetate progresses, the amount of water present becomes larger and larger, relatively to that of the salt left undecomposed, and consequently the rate of decomposition diminishes. As for the retarding effect that increase in the relative amount of water exercises, it may be explained thus. The silver in the chloracetate is converted into a chloride; we have thus, as it were, chloracetic acid striving with (potentially formed) hydrochloric acid for the possession of the silver, and the less the affinity of the latter acid for the silver, the less rapid will be

the decomposition. Now Ostwald has shown that the affinity of chloracetic acid increases rapidly with increasing dilution, whilst that of hydrochloric acid undergoes but a very slight increase; hence the effect of the addition of water is to diminish the affinity of the hydrochloric acid for the silver, relatively to that of the chloracetic acid, and, consequently, to diminish the rate of decomposition of the silver salt. C. F. B.

Periodic Law. By G. C. Schmidt (*Monatsh.*, **14**, 8—23).—The atomic volumes, melting points, and coefficients of expansion by heat of the elements are periodic functions of the atomic weights. Since each of the above properties may be assumed to depend on the number of atoms present in the solid molecule of each of the elements, it follows generally that the molecular masses of the elements are periodic functions of their atomic weight. H. C.

New System of Atomic Weights, partly based on the Direct Determination of the Molecular Weights. By A. Leduc (*Compt. rend.*, **116**, 383—386).—The system of atomic weights at present in use is in part based on the determinations of the composition of potassium chlorate, which, as Hinrichs has recently shown (this vol., ii, 163), are open to grave doubt. These atomic weights also lead to very different molecular volumes for gases which resemble one another closely in physical properties, and they do not coincide with the electrochemical equivalents. It therefore appears desirable that a new system of atomic weights should be built up, making use of direct determinations of gaseous density and of electrochemical equivalents. The author gives a list of some atomic and molecular weights determined in this manner. H. C.

New Apparatus. By A. Michael (*J. pr. Chem.* [2], **47**, 197—199).—The distillation apparatus figured below explains itself to a

great extent. The Hempel beads are contained in the neck of the flask, in order to avoid the usual prolonged column and the employment of a second cork. This necessitates a subsidiary neck in the flask for the Wurtz's air-tube. The tube which delivers into the reception chamber is provided with a three-way cock which will allow of air being let into the flask without disturbing the vacuum in the chamber; or, as here depicted, a flask may be attached to it for the collection of the largest fraction which could not be contained in the reception chamber tubes. The Y-tube, leading to the water pump, enables a vacuum to be maintained in the whole apparatus.

A slight variation on the usual form of apparatus for the determination of melting points, and a hot jacket for a funnel are also figured; the latter is provided with an inlet and an outlet tube which can either be connected with a boiler and condenser respectively, or with a hot water supply. A. G. B.

Hydrogen Sulphide Apparatus. By H. Trey (*Zeit. anal. Chem.*, **31**, 667—669).—In the *Zeit. anal. Chem.*, **31**, 183, Ostwald described a constant hydrogen sulphide apparatus, set up for the use of a students' laboratory. To prevent waste of the gas, the whole apparatus is enclosed in a box, so that nothing is accessible except a projecting brass tube, and the button of a pinch-cock, which latter, except when pressed, closes a rubber tube connecting the brass nozzle with the gas generator. M. J. S.

Inorganic Chemistry.

Amide and Imide of Sulphuric Acid. By W. Traube (*Ber.*, **26**, 607—613 (compare Abstr., 1892, 1389).—Sulphamide and sulphimide are formed when sulphuryl chloride is treated with ammonia in chloroform solution, the action being expressed by the equations—(1) $SO_2Cl_2 + 4NH_3 = 2NH_4Cl + SO_2(NH_2)_2$ and (2) $SO_2Cl_2 + 3NH_3 = 2NH_4Cl + SO_2{:}NH$. In addition to these products, Mente's imidosulphurylamide is probably produced, in accordance with the equation $2SO_2Cl_2 + 7NH_3 = 4NH_4Cl + NH(SO_2{\cdot}NH_2)_2$; although this substance was not isolated, its formation seems to be established by the fact that ammonium imidosulphonate was invariably present in the solution obtained on treating the product with water.

Sulphamide can be isolated in the following manner. Well-cooled sulphuryl chloride, diluted with 15—20 volumes of chloroform, is saturated with anhydrous ammonia, the precipitated product dissolved in water, the solution acidified with nitric acid, and the whole of the chlorine precipitated with silver nitrate; the filtered solution is neutralised with alkali, treated with silver nitrate, and the crystalline precipitate, which consists of silver sulphimide and some other silver derivative, separated by filtration. After adding a further

quantity of silver nitrate, the clear solution is treated with alkali, when silver sulphamide is obtained as a colourless, amorphous precipitate, which, however, is invariably mixed with some other silver compound, probably the same as that present in the silver sulphimide precipitate. In order to remove this impurity, the well-washed precipitate is treated with hydrochloric acid in quantity exactly sufficient to convert the silver into chloride, and the strongly acid solution is neutralised with ammonia and mixed with silver nitrate, when only the silver compound of unknown composition is precipitated; pure silver sulphamide can now be precipitated by adding silver nitrate and excess of ammonia, and on decomposing this compound with the necessary quantity of hydrochloric acid, a neutral or feebly acid solution of sulphamide is obtained.

Sulphamide is deposited in large, colourless crystals when its aqueous solution is evaporated over sulphuric acid under reduced pressure; it sinters at 75°, melts at 81°, and begins to lose ammonia at slightly higher temperatures, decomposing completely, with evolution of acid vapours, when heated above 250°. It is very readily soluble in water, its aqueous solution having a neutral reaction and a bitter taste, but it is insoluble in alcohol, ether, and other organic liquids. It is decomposed into sulphuric acid and ammonia by boiling acids, but when treated with alkalis, it is converted into sulphamic acid; it is decomposed by nitrous acid in the cold, with formation of sulphuric acid.

The *silver* derivative, $SO_2(NHAg)_2$, prepared by digesting sulphamide with ammonia and excess of silver nitrate, is a colourless, amorphous powder, only slightly sensitive to light; it has an alkaline reaction, and dissolves freely in nitric acid and ammonium carbonate, but is only sparingly soluble in cold water. It loses ammonia when heated, and decomposes completely at about 200° with evolution of sulphurous anhydride; it reacts with alkylic iodides and with acid chlorides, and its aqueous solution gives precipitates with mercuric nitrate and lead acetate.

Sulphimide, $SO_2{:}NH$, is formed, together with ammonia and imidosulphonic acid, when sulphamide is heated at 200—210°; the solid product is treated with water, the solution mixed with silver nitrate, and the precipitated silver sulphimide (*loc. cit.*) purified by recrystallisation; on decomposing the pure substance with the necessary quantity of dilute hydrochloric acid, an aqueous solution of sulphimide is obtained. This solution has a strongly acid reaction, decomposes carbonates, and, when not too concentrated, can be boiled for a short time without decomposition of the imide taking place; on evaporation even at a temperature below 40°, ammonium hydrogen sulphate remains, so that the sulphimide could not be obtained in crystals. Sulphimide is rather rapidly decomposed by warm acids, yielding sulphuric acid and ammonia, but it is only slowly acted on by excess of alkalis even on boiling. *Potassium sulphimide*, $SO_2{:}NK$, prepared by treating the silver derivative with a hot solution of the theoretical quantity of potassium chloride, forms well-defined, colourless crystals, and is not extremely soluble in water; its solution has a neutral reaction and is very stable, but is slowly decomposed by

boiling acids; the dry substance decomposes when heated, glowing vividly, and leaving a residue of potassium sulphate and sulphite, nitrogen and sulphurous anhydride being evolved. The *sodium* derivative, $SO_2{:}NNa$, is a crystalline powder, very readily soluble in water, and, like the potassium derivative, very stable. The *ammonium* derivative, $SO_2{:}N{\cdot}NH_4$, crystallises in colourless needles, and is readily soluble in water, but insoluble in alcohol; when quickly heated, it is partially converted into sulphamide, but when heated slowly, it first gives off ammonia, and then melts at about 250° with complete decomposition. The *calcium* derivative is readily soluble in water, and difficult to obtain in crystals. The *barium* derivative, $(SO_2{:}N)_2Ba + 2H_2O$, crystallises in lustrous needles, loses its water when carefully heated, dissolves freely in water, and is decomposed by boiling hydrochloric acid, barium sulphate being formed; in its aqueous solution, silver nitrate produces a very sparingly soluble precipitate. The *lead* derivative crystallises from hot dilute alcohol in long needles; the copper derivative is a green, amorphous powder.

F. S. K.

Electrical Properties of Pure Substances. I. The Preparation of Pure Nitrogen and attempts to condense it. By R. Threlfall (*Phil. Mag.* [5], **35**, 1—35).—The author has examined the processes recommended by various workers for the preparation of pure nitrogen. The method depending on the absorption of oxygen by passing air over heated copper is the most frequently mentioned; it is, however, a very objectionable one. The formation of oxides of nitrogen, the difficulty of making connection with the heated porcelain tube, and the possibility of the latter being permeable to hot furnace gases, together with the chance of a minute crack occurring in the tube and escaping detection, are amongst the mechanical disadvantages of the process. The preparation of the very pure hydrogen or carbonic oxide necessary for reducing the copper oxide presents great difficulty; if the copper absorbs sulphur, some of the latter is liable to burn out during many subsequent oxidations, and the sulphurous anhydride so formed becomes troublesome, inasmuch as no suitable reagent is known which really retains this gas. The preparation of pure nitrogen by passing air over heated phosphorus is troublesome, and there is no guarantee that the potassium permanganate, used to absorb phosphorus vapour from the resulting gas, is really efficacious; Warburg had to electrolyse the glass of his vacuum tubes in order that the nascent sodium so formed should remove the last traces of oxygen and hydrogen from the nitrogen prepared by this method, which is hence an undesirable one. Ammonium dichromate was prepared from the purest materials, and purified with the greatest care; the nitrogen obtained on heating it, however, contained nitrous compounds, for which no satisfactory absorbent is known.

The author finally adopted the method of absorbing the oxygen from air by means of copper and ammonia, the last traces of oxygen being removed by chromous chloride; the latter substance was prepared by Recoura's method (Abstr., 1886, 669), the blue solution being evaporated to a clear syrup under reduced pressure in an

atmosphere of carbonic anhydride. The gas was purified in a glass apparatus, consisting of a series of vessels containing the substances necessary for removing impurities; indiarubber was excluded, all the joints were hermetically sealed, and the glass taps ground with extreme care and sealed with mercury. The absorbing vessels used for the complete purification of the nitrogen obtained by treating dust-free air with copper and ammonia were the following:—A wash bottle containing concentrated sulphuric acid, two wash bottles and a U-tube of chromous chloride syrup, a tube of caustic potash, a tube containing silver nitrate solution with a little moist silver oxide and potassium nitrate, a tube each of potash and sulphuric acid, a U-tube containing solid potash and soda-lime in the two limbs, a bottle and three tubes exposing a large surface of phosphoric anhydride, and finally three tubes containing sulphur, silver, and copper respectively. All the substances used in the preparation were themselves carefully purified by methods which are fully discussed in the paper. The author remarks that all the samples of potash and soda examined by him, including potash obtained by exposing clean potassium to moist air, yielded traces of nitrites when dissolved. The phosphoric anhydride employed was prepared by burning phosphorus in a strong current of air; the anhydride could only be completely freed from phosphorus by distillation in a rapid stream of oxygen, which, for this purpose, was prepared in a state of great purity.

The spectrum of the nitrogen, purified in this way, was examined in a tube fitted with external electrodes. The band spectrum did not show any of the characteristic hydrocarbon or hydrogen lines; the absence of these latter gases was hence assured.

Thomson and Threlfall (Abstr., 1887, 328) observed that on passing an electric discharge through pure nitrogen the pressure diminishes; this, if due to molecular condensation of the gas, would be of considerable importance. The author therefore made a large series of experiments in order to obtain a repetition of the phenomenon; it was found, however, that the decrease of pressure was due to the formation of a nitride of mercury, probably identical with Plantamour's trimercuramine (*Annalen*, **40**, 115), by the action of the discharge on the mercury in the gauge. The compound is formed as a brown film on the glass when the electric discharge is passed over a mixture of nitrogen and mercury at about 8 mm. pressure; seven-eighths or so of the nitrogen present may be absorbed with formation of this substance, which decomposes at about 200°, and behaves as a dissociable compound on heating and cooling. It can, however, be entirely decomposed by repeated heating and cooling. No real condensation of the gas, owing to an increase in the molecular weight, can be induced at $-10°$ under a pressure of 8 mm. The appearance of the spark discharge in pure nitrogen can be changed by slight variations of temperature and, possibly, of E.M.F.; no explanation of these changes can at present be given. W. J. P.

Preparation of Nitric Oxide. By C. M. Van Deventer (*Ber.*, **26**, 589—593).—See this vol., ii, 298.

Density of Nitric Oxide. By A Leduc (*Compt. rend.*, **116**, 322—323).—Nitric oxide expelled from solutions of ferrous salts at a temperature not exceeding 40° to 50° is not completely absorbed by treatment with similar solutions. The insoluble residue amounts to 0·1 per cent., and is increased if the temperature at which the gas is expelled from the liquid is as high as 90°; it rekindles a glowing splint. Making the necessary correction, the density of nitric oxide becomes 1·0387, with a probable error of not more than a unit in the fourth decimal place. If the atomic weight of nitrogen is taken as 13·97, the ratio of the molecular volume of nitric oxide to that of oxygen is 0·99987, which seems to agree well with the critical points of the two gases. C. H. B.

Reduction of Nitric acid by Copper. By P. C. Freer and G. O. Higley (*Amer. Chem J.*, **15**, 71—81).—The pure copper having been introduced into a flask, all air is expelled by carbonic anhydride, the flask is heated to the desired temperature, and the nitric acid, heated to the same temperature, is run in. Agitation is maintained until solution is complete, when all gases are swept forward by carbonic anhydride; nitrous anhydride and nitric peroxide are absorbed by sulphuric acid; both form nitrosylsulphuric acid, but in the case of the nitric peroxide only half the nitrogen is converted into this compound, the rest appearing as nitric acid; it is thus possible, by titrating one portion of the sulphuric acid with permanganate, after Lunge (this Journal, 1877, ii, 642), and making a total nitrogen determination on the other portion in a nitrometer, to estimate the quantity of these two nitrogen oxides. The nitrous oxide, nitric oxide, and nitrogen are collected in a eudiometer, and the nitric oxide determined by addition of oxygen, and the nitrous oxide by explosion with hydrogen.

The authors arrive at the following conclusions at this stage of their investigation:—(1) The sole products of reduction of excess of nitric acid (sp. gr. 1·40) by copper are nitrous anhydride and nitric peroxide, the proportion being about 10 per cent. of the former to 90 per cent. of the latter; (2) the effect of varying temperature on the proportion of the reduction products is, apparently, but slight. They discuss these conclusions in the light of Montemartini's papers on the action of nitric acid on metals (Abstr., 1892, 1278, 1279).

A. G. B.

Amidophosphoric acid. By H. N. Stokes (*Amer. Chem. J.*, **15**, 198—214).—See this vol., i, 316.

Preparation of Pure Phosphoric acid from Sodium Phosphate, and by the Phosphorus-Nitric acid Method. By G. Watson (*J. Soc. Chem. Ind.*, **11**, 224—228).—Crystals of hydrogen sodium phosphate were subjected to the action of gaseous hydrogen chloride. In this manner, syrupy phosphoric acid, in amount corresponding with a yield of 75 per cent. of the theoretical quantity, was obtained. From the results of further trials, the author was inclined to believe that a considerable portion of the hydrogen sodium phosphate was not decom-

posed, but was simply thrown down as sodium phosphate. He then investigated the reaction more closely, using anhydrous sodium pyrophosphate instead of crystallised hydrogen sodium phosphate, and digesting it with definite weights of pure aqueous hydrochloric acid. The hydrochloric acid acts with two functions: firstly, a portion is used to saturate half the alkali in the pyrophosphate, then the remainder acts on the resulting salt, and sets free twice its weight of orthophosphoric acid. The following equation represents the final distribution of matter when equivalent quantities of sodium pyrophosphate and aqueous hydrochloric acid are digested together at the ordinary temperature:—$Na_4P_2O_7 + 4HCl + Aq = 3{\cdot}49\,NaCl + 1{\cdot}49H_3PO_4 + 0{\cdot}51HCl + 0{\cdot}51NaH_2PO_4$, whilst the expression representing the complete decomposition of the pyrophosphate by the minimum of hydrochloric acid is $Na_4P_2O_7 + 4{\cdot}685HCl + Aq = 2H_3PO_4 + 4NaCl + 0{\cdot}685HCl + Aq$. This reaction was not found to constitute a paying process for the manufacture of phosphoric acid.

It is known that on dissolving yellow phosphorus in dilute nitric acid a certain amount of phosphorous acid is produced, which amount is greater at the initial stages of the solution, and the author has attempted to determine the relative proportions of the two acids. His experiments seem to show that as the strength of the nitric acid is reduced, the ratio of the phosphorous to the phosphoric acid alters until it corresponds with that of equal weights. In the first trials, in which the strongest acids were used, it was found that reducing the time of cohobation also increased the proportion of phosphorous acid. These trials show that, in addition to the fundamental reaction, a secondary one is going on, in which the phosphorous acid formed in the primary action is being oxidised to phosphoric acid. The author concludes, from his experiments, that the balance of evidence, so far as it goes, is in favour of the statement that the primary action taking place is one in which equal weights of phosphorous and phosphoric acids are formed. In carrying out this reaction for the preparation of phosphoric acid, the author finds that it is not advisable to use an acid of greater sp. gr. than 1·250, nor one much below 1·200. By increasing the surface of the phosphorus, the speed of the reaction can be safely accelerated to a certain extent. D. B.

Crystalline Arsenates. By C. Lefèvre (*Ann. Chim. Phys.* [6], **27**, 5—62; compare Abstr., 1890, 562 and 1377).—*Barium pyroarsenate*, $2BaO,As_2O_5$, is formed when barium oxide is added to fused potassium or sodium metarsenate, or to a mixture of one of these salts with less than 40 per cent. of the corresponding chloride; on cooling very slowly, the salt is obtained in colourless, transparent plates, belonging to the orthorhombic system; when treated with cold water, it is quickly converted into the salt of the composition $2BaO,As_2O_5 + 6H_2O$. The double salt, $2BaO,K_2O,As_2O_5$, is obtained when barium oxide is added to a fused mixture of potassium pyroarsenate and potassium chloride, provided that the latter forms less than 80 per cent. of the mixture; it crystallises in colourless, transparent prisms, which become opaque when treated with cold water. When barium oxide is added to a fused mixture of sodium pyro-

arsenate and sodium chloride containing more than about 18 per cent. of the pyroarsenate, a crystalline salt of the composition $3BaO,As_2O_5$, is produced.

The salts $2SrO,As_2O_5$; $2SrO,K_2O,As_2O_5$; $2SrO,Na_2O,As_2O_5$; $3SrO,As_2O_5$; $2CaO,As_2O_5$; $2CaO,K_2O,As_2O_5$; and $2CaO,Na_2O,As_2O_5$ were prepared in a similar manner; they are all crystalline, and, in most cases, are isomorphous with the corresponding barium salts.

The double salt $4CaO,2Na_2O,3As_2O_5$ is formed when about 5 per cent. of calcium oxide is added to sodium metarsenate fused at a low temperature; it crystallises in large, transparent plates, apparently uniaxial and negative.

Lead pyroarsenate, $2PbO,As_2O_5$, prepared by saturating fused potassium metarsenate with lead oxide, crystallises in colourless plates, which slowly become opaque when treated with water; it is isomorphous with the corresponding salts of the alkali earths. The double salt, $2PbO,K_2O,As_2O_5$, is formed when lead oxide is dissolved in a fused mixture of potassium arsenate and potassium chloride, but, unless the arsenate forms more than 25 per cent., chlorine compounds are produced; it crystallises in small, transparent prisms. The corresponding sodium salt, $2PbO,Na_2O,As_2O_5$, and the compound $4PbO,2Na_2O,3As_2O_5$ were prepared.

A double salt of the composition $8CuO,K_2O,3As_2O_5$ is obtained on dissolving about 10 per cent. of cupric oxide in fused potassium metarsenate, but, in presence of a small quantity of potassium chloride, a compound of the composition $2CuO,K_2O,As_2O_5$ is formed; they both crystallise in bluish-green prisms, showing oblique extinction.

The sodium salts, $2CuO,Na_2O,As_2O_5$ and $3CuO,3Na_2O,2As_2O_5$, were prepared.

The arsenic compounds described above and in preceding abstracts (*loc. cit.*) are slowly decomposed when strongly heated in a porcelain vessel. The alkali salts are stable at a dull red heat, but at about 1000° they lose oxygen and arsenious anhydride, the expulsion of the latter being probably the result of the action of silica, since the containing vessel is vigorously attacked. Calcium pyroarsenate is decomposed at a bright red heat, but the remaining simple salts usually undergo decomposition at a dull red heat; the double salts containing both alkali and metallic oxide are decomposed less readily than the simple salts of the corresponding metallic oxides.

Ammonium magnesium arsenate is decomposed at a comparatively low temperature in a vacuum, with liberation of water and ammonia, but, at a temperature approaching to a dull red heat, pure nitrogen is evolved and arsenious anhydride sublimes; the residue contains most of the arsenic acid combined with magnesium. When the double salt is heated strongly in a stream of oxygen, traces of arsenious anhydride are almost invariably liberated, so that the calcination of the salt may give rise to errors in quantitative work.

Sodium arsenate is slowly decomposed by hydrogen at an incipient red heat, with liberation of water and arsenic; at higher temperatures, the salt is quickly acted on, and finally sodium hydroxide, containing only traces of combined arsenic, is left. Most of the other arsenates are acted on in a similar manner, and usually more readily than the

sodium salt, but sometimes, as, for example, in the cases of cobalt arsenate and nickel potassium arsenate, the expulsion of the arsenic is very incomplete, owing to the formation of an arsenide. The arsenates are also reduced by carbonic oxide at a high temperature.

F. S. K.

Preparation of Carbon under High Pressure. By H. Moissan (*Compt. rend.*, **116**, 218—224).—Experiments were made with the object of ascertaining the influence of pressure on the crystallisation of carbon at a high temperature. The various forms of carbon were isolated by successive treatment with hydrochloric or nitric acid, boiling sulphuric acid, hydrofluoric acid, and a mixture of nitric acid and potassium chlorate. Modifications of different sp. gr. were separated by means of bromal, or, more conveniently, methylene iodide, and bromoform, and mixtures of the two. The power to scratch rubies is shared by some metallic silicides, which also have a sp. gr. practically the same as that of the diamond, and hence the formation of carbonic anhydride by combustion in oxygen is necessary to characterise the latter.

When carbon is dissolved in iron between 1100° and 3000°, either graphite, or a mixture of graphite and amorphous carbon, separates on cooling under ordinary pressure, but, if the metal is allowed to cool under high pressure, the phenomena are different. A mass of iron is heated to from 2000° to 3000°, and the exterior is rapidly cooled by means of water; the still liquid interior expands as it gradually solidifies, and thus produces a very high pressure. Another method is to compress charcoal from sugar in a soft iron cylinder which is closed with a screw plug, and plunge the cylinder into a crucible containing melted wrought iron. The crucible is then withdrawn from the fire and placed in water until the exterior is cooled to a dull red heat, after which it is allowed to cool by exposure to air. Three forms of carbon are obtained, in proportions that depend on the conditions of cooling, namely, graphite, thin, contorted, maroon-coloured flakes, and diamond. The diamond is obtained as grains of grey-black *carbonado* of sp. gr. 3·0 to 3·5, and as transparent fragments with a cetaceous lustre, and parallel striæ or triangular markings. Both varieties, when burnt, leave minute quantities of ash, having all the characteristics of the ash of carbonado or diamond. The yield is, however, small, and the results are uncertain, neither diamond nor carbonado being obtained in many of the experiments.

Similar results can be obtained, although with even greater uncertainty, by dissolving carbon in iron melted at about 2000°, and rapidly cooling the metal in a current of coal gas.

Silver expands when solidifying, and also has the power of dissolving carbon. If a quantity of the metal is heated to boiling in a crucible brasqued with charcoal, and then rapidly cooled on the outside by immersing it in water, carbonado is obtained in small plates of sp. gr. from 2·5 to 3·5.

The silver used in these experiments contained a very small quantity of gold, and some of the grains of carbon were impregnated with this metal. Des Cloizeaux has observed that some specimens of natural carbonado enclose small globules of gold. C. H. B.

Reproduction of Diamonds, By C. FRIEDEL (*Compt. rend.*, **116**, 224—226).—When carbon bisulphide is placed in a cavity cut in a block of mild steel and closed with a screw, and the whole is heated to dull redness or to bright redness, the bisulphide decomposes, leaving a residue of amorphous carbon, whilst the interior of the cavity is lined with a thin film of iron sulphide and the remainder of the sulphur is diffused throughout the steel to a distance of more than 15 mm. from the cavity.

If sulphur is heated in closed vessels at 500° with cast-iron turnings rich in carbon, and the product is treated with acids and finally with a mixture of nitric acid and potassium chlorate, a very small quantity of residue is left, in the form of a black powder which scratches corundum, but the quantity obtained was insufficient for analysis.

C. H. B.

Potassium-astrachanite, a new Potassium-magnesium Double Sulphate. By J. K. VAN DER HEIDE (*Ber.*, **26**, 414).—This substance, $MgSO_4,K_2SO_4 + 4H_2O$, is formed when a solution of schönite ($MgSO_4,K_2SO_4 + 6H_2O$) and sodium chloride is evaporated at 60° or from a solution of magnesium and potassium sulphates at 100°. It crystallises in tables, and is the potassium analogue of the already known sodium compound, astrachanite. C. F. B.

Calcium Oxychloride. By B. ZAHORSKY (*Zeit. anorg. Chem.*, **3**, 34—43).—This substance is prepared by boiling lime with a concentrated solution of calcium chloride, or by dissolving excess of lime in hydrochloric acid, filtering, and allowing to cool. The salt crystallises in long, thin needles, which are lustrous, highly refractive, and transparent when fresh, but, if kept in the air, take up carbonic anhydride and become opaque. It dissolves in glycerol, but is decomposed by water, alcohol, and other solvents. It decomposes ammonium chloride with liberation of ammonia. Several analyses of the substance have already been made; those of the author agree well with the composition $3CaO,CaCl_2 + 15H_2O$. Probably the constitutional formula is HO·Ca·O·Ca·Cl + $7H_2O$, for only 14 out of the 15 mols. of water are lost by drying in a vacuum.

The following table gives the grams of lime which dissolve at different temperatures in 100 c.c. of pure water, or of aqueous calcium chloride solutions of varying strength. In the cases marked *, a certain quantity of calcium chloride was precipitated from the solution as oxychloride.

Temp.	Pure water.	$CaCl_2$, 5 p. c.	$CaCl_2$, 10 p. c.	$CaCl_2$, 15 p. c.	$CaCl_2$, 20 p. c.	$CaCl_2$, 25 p. c.	$CaCl_2$, 30 p. c.
20°	0·1374	0·1370	0·1661	0·1993	0·1857*	0·1661*	0·1630*
40	0·1162	0·1160	0·1419	0·1781	0·2249	0·3020*	0·3684*
60	0·1026	0·1020	0·1313	0·1706	0·2204	0·2989	0·3664
80	0·0845	0·0936	0·1328	0·1736	0·2295	0·3261	0·4122
100	0·0664	0·0906	0·1389	0·1842	0·2325	0·3710	0·4922

C. F. B.

Constitution of Bleaching Power. By G. LUNGE (*Zeit. anorg. Chem.*, **2**, 311—313).—The author calls attention to the fact that the reactions of bleaching powder, recently observed by Mijers (this vol., ii, 209), form an independent confirmation of the results previously published by him, and are likewise best explained by assuming that the compound has the formula attributed to it by Odling.

G. T. M.

Monomagnesium Phosphate. By J. STOKLASA (*Zeit. anorg. Chem.*, **3**, 67—75; compare this vol., ii, 168).—This salt, $MgH_4(PO_4)_2 + 2H_2O$, is decomposed at different temperatures in the manner represented by the following equations.

$$4MgH_4(PO_4)_2,2H_2O$$

$$\text{At } 100—170° = 4MgH_4(PO_4)_2 + 8H_2O,$$

$$175—176° = 3MgH_4(PO_4)_2 + MgH_2P_2O_7 + 9H_2O,$$

$$183—184° = 2MgH_4(PO_4)_2 + 2MgH_2P_2O_7 + 10H_2O,$$

$$196° = 4MgH_4(PO_4)_2 + 3MgH_2P_2O_7 + 11H_2O,$$

$$205° = MgH_2P_2O_7 + 12H_2O,$$

$$210—303° = 4Mg(PO_3)_2 + 16H_2O.$$

It is not decomposed by water, even at 60°. Absolute and aqueous alcohol both decompose it completely at 100°, if in large excess, according to the equation

$$MgH_4(PO_4)_2,2H_2O + H_2O = MgHPO_4,3H_2O + H_3PO_4.$$

The dimagnesium phosphate thus obtained has been hitherto unknown; it forms crystals with a nacreous lustre, and dissolves sparingly in water, readily in acids. C. F. B.

Preparation of Sulphites of Zinc, Manganese, and Cadmium. By G. DENIGÈS (*Bull. Soc. Chim.* [3], **7**, 569—573).—Zinc sulphite, $ZnSO_3 + 2\frac{1}{2}H_2O$, is prepared by mixing in the cold 25 per cent. solutions of zinc sulphate and sodium sulphite, the first acidified with acetic acid, when it separates, after 12—15 hours, in clinorhombic prisms.

Manganese sulphite, $MnSO_3 + 3H_2O$, obtained by mixing 10 per cent. solutions of manganese sulphate acidified with acetic acid and sodium sulphite, crystallises in oblique prisms; whilst a monohydrate, which is formed when the additive compound $MnSO_3,2NH_2Ph,H_2SO_3$ is dissolved in boiling water, crystallises in rhombic prisms.

Cadmium sulphite, $CdSO_3 + 3H_2O$.—This salt separates on mixing equal volumes of 10 per cent. solutions of cadmium sulphate acidified with acetic acid and sodium sulphite. The author failed to obtain Muspratt's dihydrate (*Phil. Mag.* [3], **30**, 414). A. R. L.

Stas's Determinations of the Atomic Weight of Lead. By G. HINRICHS (*Compt. rend.*, **116**, 431—433).—According to the author, the determinations of the atomic weight of lead by Stas contain the same systematic error that exists in the determinations of the oxygen in potassium chlorate (this vol., ii, 163). The values obtained for the atomic weight are functions of the amounts of lead used in the deter-

minations. The proof for this case is not, however, so convincing a one as that for the chlorate. H. C.

Mixed Double Haloïds of Lead and Potassium. By C. H. HERTY (*Amer. Chem. J.*, **15**, 81—104; compare Abstr., 1892, 779).—The crystals obtained by cooling hot solutions of lead bromide in potassium iodide, and by crystallising cold solutions of the same, all proved to be the salt $KPbI_3 + 2H_2O$. By dissolving lead iodide in an aqueous solution of potassium bromide, two classes of crystals were generally obtained: needle-shaped crystals, which proved to be isomorphous mixtures of $KPbI_3 + H_2O$ and $KPbBr_3 + H_2O$, and tabular crystals which were mixtures of varying proportions of potassium lead iodide, $KPbI_3$, potassium lead bromide, $KPbBr_3$, and lead bromide. The existence of such mixed double haloïds as $KPbI_2Br$ and $KPbIBr_2$ has, therefore, not yet been proved. (Compare Richardson's conclusion, Abstr., 1892, 784.) A. G. B.

Thallium Sulphite. By K. SEUBERT and M. ELTEN (*Zeit. anorg. Chem.*, **2**, 434—436).—On mixing solutions of thallium sulphate and sodium sulphite, *thallium sulphite* is precipitated as a white, granular, crystalline powder. It is insoluble in alcohol, but dissolves readily in warm water, and the solution, on being slowly cooled, deposits the salt in the form of feathery aggregates of slender needles. At 15·5°, 100 parts of water dissolve 3·34 parts of the salt. Its sp. gr. at 19·8° is 6·4273. G. T. M.

Graphochemical Calculation. By E. NICKEL (*Zeit. physikal. Chem.*, **11**, 265—274).—The principles described and employed in previous papers (Abstr., 1892, 1158; this vol., ii, 115 and 119) are applied to the discussion of the different processes involved in the reduction of copper from its ores. H. C.

Action of Potassium Iodide or Sodium Thiosulphate on Mercurammonium Salts. By E. BALESTRA (*Gazzetta*, **22**, ii, 557—563).—Mercurammonium salts are dissolved by potassium iodide or sodium thiosulphate solutions with liberation of ammonia and alkali, in accordance with the following equations:—

$$NHg_2I + 3KI + 3H_2O = 2HgI_2 + NH_3 + 3KOH.$$
$$NHg_2I + 2Na_2S_2O_3 + 3H_2O = 2HgS_2O_3 + NaI + NH_3 + 3NaOH.$$

The author has performed these reactions for a number of mercurammonium salts, and determined the ammonia by distillation and the remaining alkali by direct titration; the results obtained agree well with the theoretical values. Similar reactions occur in the case of double salts such as NHg_2Cl,NH_4Cl. W. J. P.

Decomposition of Alkali Aluminates in presence of Alumina. By A. DITTE (*Compt. rend.*, **116**, 183—185).—When crystallised potassium aluminate is dissolved in water, it partially decomposes with separation of alumina. If the solution is filtered after a few minutes, it is limpid, but if kept in a closed vessel, it gradually de-

composes with separation of alumina, which attaches itself to the sides of the vessel in the form of a strongly adherent crust of small, transparent crystals of the same composition as gibbsite, $Al_2(OH)_6$.

The same decomposition can be observed if a solution of any aluminium salt is mixed with potassium hydroxide in quantity not quite sufficient to redissolve the precipitated aluminium hydroxide.

A solution containing a very slight excess of potassium hydroxide above that required to dissolve the aluminium hydroxide will remain clear for many months.

When the quantity of alkali is not quite sufficient to keep the whole of the alumina in solution, a condition of equilibrium is established between the aluminate, the alumina, the alkali hydroxide, and the water. Any local variation of temperature disturbs this equilibrium, and a small quantity of alumina separates and crystallises in the form of gibbsite. This crystallised form is less soluble than the gelatinous form, and does not redissolve even when the temperature reverts to its original value. Consequently there is a further disturbance of the equilibrium, more alumina separates, and in contact with the gibbsite already formed, crystallises and becomes less soluble, and this change goes on until equilibrium is established between the aluminate, the alkali hydroxide, water, and gibbsite.

The accuracy of this view is proved by the fact that anything that promotes contact of the solution with the separated alumina accelerates the change and *vice versâ*. The phenomena and the explanation of them are the same in the case of sodium hydroxide.

C. H. B.

Decomposition of Alkali Aluminates by Carbonic Anhydride. By A. Ditte (*Compt. rend.*, **116**, 386—388).—When potassium carbonate solution is added drop by drop to a solution of potassium aluminate, a precipitate forms and at first redissolves, but afterwards becomes permanent; it has the composition $3K_2O,Al_2O_3,5CO_2$. Potassium hydroxide is formed at the same time, and since it is capable of decomposing the double carbonate, a condition of equilibrum is established.

When carbonic anhydride is allowed to fall on the surface of a solution of potassium aluminate containing a small excess of alkali, potassium carbonate is formed, but no precipitation of the double carbonate takes place until the greater part of the excess of alkali has been neutralised. At this point, the water decomposes a small quantity of the aluminate, and the liberated alumina dissolves at first in the potassium hydroxide, but quickly separates in crystals of the hydroxide, $Al_2(OH)_6$; there can no longer be equilibrium, and the aluminate decomposes more or less rapidly.

If carbonic anhydride is passed into a similar solution until a permanent precipitate of the double carbonate and the crystallised hydroxide begins to form, and the flask is then closed, a heavy precipitate of the double carbonate at first settles, but is gradually decomposed by the potassium hydroxide liberated by the decomposition of the aluminate by water, and crystallised aluminium hydroxide separates.

If the solution of the aluminate contains a considerable excess of alkali, and carbonic anhydride is passed into it until a permanent precipitate begins to form, and the flask is then closed, a precipitate

of the double carbonate separates, but as there is still sufficient potassium hydroxide in the liquid to prevent decomposition of the aluminate, crystallised aluminium hydroxide is not formed. A similar result is obtained if potassium carbonate is first added to the solution until the precipitate redissolves with difficulty, and carbonic anhydride is then passed into the liquid until a permanent precipitate is formed. In both cases, if the passage of the carbonic anhydride is continued too long, too much of the alkali is neutralised and the aluminate gradually decomposes. C. H. B.

Action of Hydrogen Ammonium Sulphate on Glass. By M. Lachaud and C. Lepierre (*Bull. Soc. Chim.* [3], **7**, 603—608).—Weighed pieces of glass rod, 20 mm. in length, were heated for 60 hours with an excess of fused hydrogen ammonium sulphate, the salt being renewed as it volatilised, the glass finally washed with hot water, and the loss in weight determined. A sample of ordinary soda-lime glass lost as much as 21·5 per cent. of its weight; it had then the appearance of porcelain, and could be reduced to powder under the pressure of the hand. By analyses of the sample before and after this treatment, the loss was found to be mainly due to sodium oxide; it amounted to 20 per cent. of sodium oxide out of 22 per cent. originally present. When heated with concentrated sulphuric acid for 40 hours, the same glass lost only 0·05 per cent. On fusion with hydrogen ammonium sulphate, Bohemian glass lost 12 per cent., and crystal glass 10 per cent., of their weight, 10 and 8 per cent. respectively of which represented potassium oxide. The authors find that by fusing together a mixture of potassium sulphate and ammonium hydrogen sulphate, 9 per cent. of the potassium sulphate is volatilised with the ammonium salt. A. R. L.

Action of Water Vapour on Ferric Chloride. By G. Rousseau (*Compt. rend.*, **116**, 188—190).—When anhydrous ferric chloride is heated in a glass tube in a slow current of carbonic anhydride saturated with aqueous vapour, brownish-red needles of the oxychloride $Fe_2Cl_6,2Fe_2O_3$ are formed between 275° and 300°, and darker and larger needles of the oxychloride $Fe_2Cl_6,3Fe_2O_3$. It follows that the decomposition of ferric chloride in presence of water vapour is strictly analogous to its decomposition in concentrated solutions (Abstr., 1892, 119—120). Between a dull red heat and the softening point of glass, no sublimate is formed when the ferric chloride is in excess, but hexagonal lamellæ of hematite are obtained when the water vapour is in excess. The non-formation of an oxychloride or the oxide at a dull red heat when the chloride is in excess is probably due to the occurrence of some reverse reaction. C. H. B.

Mixed Crystals of Ammonium and Ferric Chlorides. By J. L. C. Schroeder van der Kolk (*Zeit. physikal. Chem.*, **11**, 167—173).—The observations of Roozeboom (Abstr., 1892, 1384) on mixed crystals of ammonium and ferric chlorides have been extended by the author, and mixed crystals of ammonium chloride with the chlorides of cobalt, nickel, and cadmium also examined. A detailed description

of the appearance of some of the crystals is given. The author considers it probable that the ferric chloride crystals are isomorphous mixtures of ammonium chloride with a regular modification of ferric chloride, perhaps $Fe_2Cl_6,8H_2O$. In the other cases, isomorphous mixtures are probably not formed. H. C.

Preparation of Chromium and Manganese at a High Temperature. By H. Moissan (*Compt. rend.*, **116**, 349—351).—When manganous oxide is mixed with charcoal and heated in the arc formed by a current of 60 volts and 300 ampères, reduction is complete in 5 or 6 minutes; with 50 volts and 100 ampères, reduction requires 12 to 15 minutes. In presence of excess of carbon, the reduced metal contains 6·4 to 14·6 per cent. of that element, but in presence of excess of manganous oxide, the reduced metal contains only 4 to 5 per cent. of carbon. When the proportion of carbon is low, the metal remains unaltered even in open vessels, but with a higher proportion of carbon, it is attacked by atmospheric moisture. Small fragments placed in water are completely attacked in 24 hours, hydrogen and hydrocarbons being given off.

Chromium oxide mixed with carbon is reduced in from 8 to 10 minutes with a current of 50 volts and 350 ampères, about 100 grams of the metal being obtained. With 50 volts and 100 ampères, reduction requires about 15 minutes. The proportion of carbon in the reduced metal varies from 8·6 to 12·85 per cent., but if this product is broken up, placed in a carbon crucible brasqued with chromic oxide, covered with the same oxide and again subjected to the action of the arc, metallic chromium is obtained quite free from carbon.

Chrome iron ore can be reduced in the same manner, a homogeneous alloy of chromium and iron being obtained. C. H. B.

Crystalline Forms of Chromium and Iridium. By W. Prinz (*Compt. rend.*, **116**, 392—395).—Chromium prepared by Woehler's method forms minute cubes with pyramidal faces, the symbol being, approximately, $b^{\frac{4}{3}}$, this form giving rise to the hexagonal and octagonal contours seen when the powder is examined by transmitted light. The rhombohedra described by previous observers are very probably deformed octahedra.

Iridium prepared by Stas in the form of a highly lustrous powder was seen under the microscope to consist of regular hexagonal lamellæ, triangles, small crosses, and regular octahedra. All the other forms are derived from the regular octahedron, the triangles being flattened tetrahedra, whilst the hexagons arise from the deformation of the octahedron along one of its faces. All the forms closely resemble the crystallites of copper observed in aventurine. It follows that, so far as Stas's preparation shows, iridium is not dimorphous and does not crystallise in the hexagonal (rhombohedral) system.

C. H. B.

Chromium Fluorides. By C. Poulenc (*Compt. rend.*, **116**, 253—256).—*Chromous fluoride*, CrF_2, is obtained by the action of gaseous hydrogen fluoride on metallic chromium at a red heat, or by the action of the same gas on chromous chloride at the ordinary tempe-

rature. After fusion it forms a transparent green mass, with a nacreous lustre, and a very brilliant, lamellar, crystalline fracture; sp. gr. 4·11. It is insoluble in alcohol, and only slightly soluble in water, dissolves in boiling hydrochloric acid, is very slightly attacked by nitric acid, and is but slowly attacked even by boiling sulphuric acid. It is reduced by hydrogen at a dull red heat, and when heated in the air is converted into chromic oxide. At a red heat, it is decomposed by hydrogen chloride, by water vapour with formation of hydrogen fluoride and chromic oxide, and by hydrogen sulphide with formation of black chromium sulphide and hydrogen fluoride. Fused potassium nitrate attacks chromous fluoride readily with formation of normal potassium chromate; fused alkali carbonates first convert it into an alkali fluoride and chromium oxide, whilst at a higher temperature a normal chromate is formed.

Chromic fluoride, Cr_2F_6, is obtained in a crystalline form by the action of gaseous hydrogen fluoride on anhydrous chromic chloride, precipitated chromic oxide, hydrated chromic fluoride, or amorphous anhydrous chromic fluoride.

When chromic chloride is heated to dull redness in hydrogen fluoride, anhydrous chromic fluoride is formed, and if the tube is heated at 1200°, part of the product volatilises, and condenses in very slender needles, whilst the non-volatilised portion solidifies to a deep green mass, on the surface of which are long, well-defined, highly refractive, green prisms. All three forms have the same composition. C. H. B.

Complex Inorganic Acids. By F. Kehrmann (*Zeit. anorg. Chem.*, **3**, 76—77).—Under certain circumstances, to be described later, reddish-yellow phosphomolybdates have been obtained; the potassium and ammonium salts dissolve readily in water. The corresponding acid has been obtained in the free state.

C. F. B.

Molybdoarsenates. By C. Friedheim (*Zeit. anorg. Chem.*, **2**, 314—410; compare Abstr., 1890, 1066; 1891, 884).—A number of molybdoarsenic acids were prepared by Pufahl, by the addition of sulphuric acid to a mixture of barium molybdate and arsenic acid, and salts of the same acid were obtained by boiling together solutions of the alkali arsenates and molybdic acid. On heating a solution of potassium arsenate, KH_2AsO_4, with molybdic anhydride, several products are formed. The first has the composition $K_2O,As_2O_5,6MoO_3 + 5H_2O$, and is identical with one of the compounds obtained by Pufahl in the above-mentioned way. It forms characteristic, microscopic, octahedral crystals. The second product forms rhombohedral crystals, having the composition $3K_2O,As_2O_5,18MoO_3 + 26H_2O$, and is identical with the compound obtained by the addition of potassium carbonate to an aqueous solution of the red-coloured molybdoarsenic acid $As_2O_5,18MoO_3 + 28H_2O$, which is the third well-characterised product of the action. In a similar way, this acid and the salt $3Na_2O,As_2O_5,18MoO_3 + 24H_2O$ were obtained from monosodium arsenate. The nature of the pro-

ducts in all these cases depends not only on the quantity of molybdic anhydride employed, but also on the nature of the alkali arsenate. When dipotassium arsenate and molybdic anhydride are allowed to interact in molecular proportion, the compound $3K_2O,As_2O_5,6MoO_3 + 25H_2O$ is obtained, and the sodium salt, $3Na_2O,As_2O_5,6MoO_3 + 11H_2O$, is formed in a similar way. On employing a large excess of molybdic acid, the compound $3K_2O,As_2O_5,24MoO_3 + 12H_2O$, previously prepared by Pufahl, is obtained. In short, all the compounds previously prepared, in addition to several new ones, are to be obtained directly from their components. The author discusses, at length, the considerations which have led him to ascribe the formula $AsO(OH)_2{\cdot}O{\cdot}MoO_2{\cdot}O{\cdot}MoO_2{\cdot}O{\cdot}MoO_2{\cdot}OK$ to the compound

$$K_2O,As_2O_5,6MoO_3,$$

and the constitution $AsO(O{\cdot}MoO_2{\cdot}O{\cdot}MoO_2{\cdot}O{\cdot}MoO_2{\cdot}OK)_3$ to the compound $3K_2O,As_2O_5,18MoO_3$. By substituting the groups $Mo(OH)_4$ for MoO_2 in these formulæ, it is possible also to account for the water molecules existing in the compounds. G. T. M.

Preparation of Uranium at a High Temperature. By H. Moissan (*Compt. rend.*, **116**, 347—349).—The mixture of oxides obtained by strongly heating uranium nitrate is mixed with a slight excess of carbon, and strongly compressed into a carbon crucible, which is then embedded in magnesia, and subjected in an electrical furnace to the arc formed by a current of 60 volts and 450 ampères. Reduction takes almost immediately, and an ingot of 200 to 220 grams is obtained in 12 minutes. The metal is very hard, and has a brilliant fracture; it is not pure, but contains from 5 to 13·5 per cent. of carbon. Its melting point is higher than that of platinum, but it decomposes water at the ordinary temperature. C. H. B.

The Determination of Equivalents by Conversion of Oxides into Sulphates. The Separation of the Gadolinite Metals. By G. Krüss (*Zeit. anorg. Chem.*, **3**, 44—59).—Attention is called to the fact that the presence of impurities, even when as much as 1 per cent., cannot always be detected by the spectroscope, and in the case of compounds of the rare earths, the use of quantitative analysis is recommended, in order to ascertain if two successive fractions are identical or different. Of the various methods, the author prefers the conversion of an oxide into a sulphate by treating it in a crucible with dilute sulphuric acid, evaporating, and then igniting gently, at about 350°. The method is trustworthy, and no basic sulphate is formed; Bailey's statement (Trans., 1887, 676) that no constant weight can be obtained is shown by experiment to be incorrect. The use of a porcelain crucible is admissible.

At the end of the paper is given a synopsis of the methods at present in use for separating metals of the cerium and ytterbrium groups. It is too long to reproduce here; but the following are the heads under which the methods are arranged:—I. Crystallisation of double salts. II. Precipitation of basic salts. III. Fractional pre-

cipitation of the earths in various forms. IV. Fractional solution. V. Oxidation (only in case of cerium). C. F. B.

Electrolysis of Solutions of Metals of the Rare Earths. By G. KRÜSS (*Zeit. anorg. Chem.*, **3**, 60—62).—If a solution containing chlorides of the rare earth metals is electrolysed, hydrogen and chlorine are evolved at the two poles, and the oxides of the metals are precipitated. It is obvious that the last metal to separate out will be that one which has the greatest tendency to combine with chlorine, and it should be possible to effect at least a partial separation of the metals by fractional electrolysis. An experiment actually showed that, when a mixture was precipitated in three fractions with aniline, and the middle fraction again separated into five by fractional electrolysis, the electrolysis effected a separation in the same sense as the precipitation. The vessel used was a beaker of 15 cm. diameter; inside it, and touching the glass, was a cylinder of copper gauze reaching to the top of the liquid, and forming the negative electrode; the positive electrode was a rod of gas carbon placed in the axis of the beaker. The battery contained four Bunsen elements joined in series. C. F. B.

Double Halogen Compounds of Gold. By G. KRÜSS and F. W. SCHMIDT (*J. pr. Chem.* [2], **47**, 301—302).—The authors cannot admit that $AuBr_2$ or Au_2Br_4 is produced by the action of bromine on gold under the conditions of Thomsen's experiments (Abstr., 1888, 559). They are not convinced by Petersen's arguments (this vol., ii, 126), and still maintain that $AuBr_3$ is the ultimate product of the action of bromine on gold. A. G. B.

Rapid Reduction of Potassium Platinochloride. By H. BORNTRÄGER (*Zeit. anal. Chem.*, **32**, 188).—The precipitate is dissolved in hot water and potassium oleate added. This produces a precipitate containing 58 per cent. of oleïc acid, 23 per cent. of platinum, and 19 per cent. of potassium chloride. Ignited for a few minutes, it decomposes very readily, leaving a mixture of very active platinum black with potassium chloride; the latter can be removed by washing with hot water. M. J. S.

Atomic Weight of Palladium. By A. JOLY and E. LEIDIÉ (*Compt. rend.*, **116**, 146—148).—Pure palladium was converted into potassium palladionitrite, and the latter into potassium palladiochloride, which was carefully recrystallised, and dried at 100°. It was then electrolysed in aqueous solution acidified with hydrochloric acid, the deposited metal being heated in a current of hydrogen, and allowed to cool in a current of carbonic anhydride; as a mean of eight determinations, Pd = 105·438, when H = 1, O = 15·96, and Cl = 35·37. This value is almost identical with that obtained by Bailey and Lamb, 105·459 (Trans., 1892, 745—753).

Reduction of the palladiochloride in hydrogen gave, as a mean result of two experiments, Pd = 105·665, but the experiments are being continued. C. H. B.

Physical Properties of Fused Ruthenium. By A. Joly (*Compt. rend.*, **116**, 430—431).—Ruthenium can be fused and obtained in ingots of 25 to 30 grams by means of the electric arc. In order to avoid volatilisation as far as possible, the metal should be heated very rapidly. The metal, after treatment with aqua regia and hydrofluoric acid, is heated in hydrogen to reduce the superficial film of oxide. It then has a grey colour, more like that of iron than of platinum, its hardness is comparable to that of iridium, and it is brittle when cold, but somewhat malleable at a red heat. The sp. gr. of the fused and powdered metal at 0°, compared with water at 4°, is 12·063.

C. H. B.

Mineralogical Chemistry.

Origin of the Diamond. By J. Werth (*Compt. rend.*, **116**, 323—326).—Consideration of the mode of occurrence, crystalline form and aspect, and the general physical and chemical properties of the diamond leads the author to conclude that diamonds have been formed under pressure at a high temperature in presence of hydrogen containing more or less carbon, and have been cooled rapidly. Bort contains 0·5 per cent. of hydrogen, and when heated under water, gives off bubbles of gas. C. H. B.

Graphite, Carbonado, and Microscopic Diamonds in Blue Earth from the Cape. By H. Moissan (*Compt. rend.*, **116**, 292—295).—Blue earth from De Beer's Mine was treated with boiling sulphuric acid for several hours, washed, treated with aqua regia, and again washed. It was then subjected to repeated alternate treatment with hydrofluoric and sulphuric acids. 2 kilos. of the earth left only a very minute quantity of a residue containing brilliant, hexagonal or lamellar crystals of graphite which yielded a greenish graphitic oxide when treated in the usual way, together with microscopic grains of carbonado and diamonds, mixed with amber-yellow grains and long, transparent, non-combustible prisms, both of which can be decomposed by fusion with potassium hydrogen sulphate and subsequent treatment with hydrofluoric and sulphuric acids. Carbonado has previously been detected in the blue earth by Couttolenc, who, however, did not recognise the presence of microscopic diamonds.

C. H. B.

Cupro-iodargyrite, a new Mineral. By H. Schulze (*Chem. Zeit.*, **16**, 1952).—Among some minerals from the San Agustin Mine, Iquique, Chili, the author found specimens of a copper silver iodide, hitherto not observed in nature. The new mineral has a sulphur-yellow colour with an adamantine lustre. On analysis, it yielded the following results:—

C.	Ag.	I.
15·91	25·58	57·75

These results are in accord with those demanded by the formula CuI,AgI (compare Abstr., 1891, 1436). B. H. B.

Cuproplumbite from Butte City, Montana. By J. T. De Bell (*Amer. Chem. J.*, **14**, 620—621).—An analysis of this substance gave—

Cu.	Pb.	S.	SiO_2.	Total.
61·32	18·97	17·77	1·58	99·64

This agrees approximately with the formula $5Cu_2S,PbS$. The mineral is amorphous, of bluish-grey-black colour, lustre submetallic, fracture uneven, fuses with spirting, sp. gr. = 5·39, hardness = 2·5. From considerations regarding its specific gravity, it is classed rather with galena than with chalcosite. C. F. B.

Platiniferous Nickel Ore from Canada. By F. W. Clarke and C. Catlett (*Chem. News*, **67**, 53—54; from *Bull. U.S. Geol. Surv.*, No. 64).—An analysis of nickel ore from the mines at Sudbury, Ontario, gave the following results:—

Ni.	Fe.	SiO_2.	Cu.	S.	Total.
41·96	15·57	1·02	0·62	40·80	99·97

These figures correspond approximately with the formula Ni_3FeS_3. In short, the mineral has the composition Ni_4S_5, with about one-fourth of the nickel replaced by iron. The only known species with which this agrees is Laspeyres's polydymite, of which the Sudbury mineral is evidently a ferriferous variety. The peculiarity of this ore is that it contains platinum in appreciable quantities, three specimens of the Sudbury ore assayed showing respectively 0·0087, 0·006, and 0·024 per cent. of platinum. Probably the platinum exists in the ore as sperrylite. B. H. B.

Brazilite. By E. Hussak (*Jahrb. f. Min.*, 1893, i, Mem. 89).—An analysis of the monoclinic mineral brazilite by C. W. Blomstrand showed that it consists of pure zirconia, the analytical results being as follows:—

ZrO_2.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Alkalis.	Loss.	Total.
96·52	0·70	0·43	0·41	0·55	0·10	0·42	0·39	99·52

B. H. B.

Statuary Marble from Rutland, Vermont. By J. T. De Bell (*Amer. Chem. J.*, **14**, 626—627).—This marble is very pure, containing as impurities only the following percentage amounts:—SiO_2, 0·167; Fe_2O_3 and Al_2O_3, 0·062; Na_2O, 0·065; K_2O, 0·004; MgO, 0·079. The lime prepared from it is but little inferior to that from Carrara marble, if required for the separation, in analysis, of magnesia from alkalis. C. F. B.

Electrical Calamine from Wythe Co., Virginia. By A. Jones (*Amer. Chem. J.*, **14**, 621).—A peculiarly pure specimen of

$ZnSiO_4 + H_2O$. It occurs occasionally as a layer of bright, transparent, colourless crystals, encrusting to a depth of 1—2 mm. the snow-white opaque sheets of the ordinary ore. C. F. B.

The Mesotype Group in the Puy-de-Dôme. By F. GONNARD (*Jahrb. f. Min.*, 1893, i, Ref. 247; from *Bull. soc. fran. min.*, **14**, 165—174).—The zeolite described by Guilleruin as mesotype from the Puy-de-Dôme is shown by analysis to be scolezite. It was, however, probably not derived from the Puy-de-Dôme, for all the mesotypes of this district examined by the author are shown to be natrolite. The following are the results of two analyses, I, mesotype from the Puy-de-Marman, and II, from the Tour de Gevillat:—

	SiO_2.	Al_2O_3.	Na_2O.	CaO.	H_2O.	Total.
I.	48·03	26·68	15·61	—	9·62	99·94
II.	47·88	26·12	15·63	0·45	9·80	99·88

B. H. B.

Paranthrite from Clay Co., N. Carolina. By W. N. BERKELEY (*Amer. Chem. J.*, **84**, 628).—This mineral occurred in a corundum mine, in a pocket near the centre of a 6-foot vein, consisting of decomposed albite, corundophilite, and chloritic minerals, lying between chrysolite and horblende gneiss. It consists of bluish-grey, rounded, crystalline lumps; sp. gr. = 2·75, hardness = 5·5, composition:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.
47·54	34·03	17·23	1·82	1·02

C. F. B.

Glauconite from Hanover Co., Virginia. By M. B. CORSE and C. BASKERVILLE (*Amer. Chem. J.*, **14**, 627—628).—This occurs in a bed of greensand marl. It appears as rounded grains interspersed with seams of quartz and with some spots of a much deeper green colour than the main portion. It is almost insoluble in strong acids, but after gentle ignition, when it turns brown, it is completely gelatinised by hydrochloric acid. II has a sp. gr. = 2·83, fusibility = 4·5.

	SiO_2 comb.	Quartz.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	K_2O.
I.	43·34	8·22	6·62	15·16	8·33	0·95	0·62	4·15
II.	47·43	2·76	7·33	12·03	9·43	2·90	0·57	5·75

	Na_2O.	H_2O.	Total.
I.	1·84	10·32	99·55
II.	0·42	9·85	98·49

C. F. B.

Constitution of Spherulites in Acid Eruptive Rocks. By W. CROSS (*Jahrb. f. Min.*, 1893, i, Ref. 294—297; from *Bull. Phil. Soc. Washington*, **11**, 411—444).—The author regards microfelsite as a mechanical mixture of quartz and felspar (chiefly orthoclase) in varying quantities. Among the spherulites in the rocks of Rosita Hills and Silver Cliff, he has not found one that is not composed of definite minerals. Analysis of two obsidians, from Silver Cliff, with large

spherulites, and from Rosita Hills, shows that the glass consists almost exclusively of alkalis and alumina (in the felspar ratio), silicic acid, and water. B. H. B.

The Meteorite from Cañon Diablo. By H. Moissan (*Compt. rend.*, **116**, 288—290, and C. Friedel, *ibid.*, 290—991).—Part of the meteorite from Cañon Diablo (Abstr., 1892, 284, 497; this vol., ii, 174), when treated with hydrochloric acid until all the iron was dissolved, left a residue of carbon in the form of an impalpable powder, thin maroon-coloured plates, similar to those obtained from iron cooled under pressure, and rounded fragments of high density. The latter, when treated with nitric acid and potassium chlorate, left two yellowish fragments, with a fatty lustre and a general appearance recalling the contorted crystallisation of bort. They scratched ruby easily, and one of them when burnt in oxygen yielded carbonic anhydride. The larger of the two fragments measured 0·7 by 0·3 mm. The denser carbon was associated with a grey substance in dendritic masses, which somewhat resembled platinum, but was not attacked by aqua regia. The meteorite is very far from being uniform in composition, considerable differences being observed in parts not more than 10 mm. distant from one another.

Friedel has not found in the same meteorite such large fragments of diamond, but has recognised amongst the microscopic grains of carbonado that he obtained, a certain number of small, transparent grains, which are, doubtless, white diamond. The dendritic substance is an iron sulphide, the composition of which corresponds with the formula Fe_3S. C. H. B.

Physiological Chemistry.

Elimination of Carbonic Oxide. By L. de Saint-Martin (*Compt. rend.*, **116**, 260—263).—When a rabbit partially poisoned by carbonic oxide, is placed under such conditions that natural elimination is impossible, as in a Regnault and Reiset's apparatus filled with air containing a known quantity of carbonic oxide, a certain quantity of the gas is slowly but regularly destroyed, the destruction taking place more actively the smaller the quantity of carbonic oxide that the animal has inhaled.

In estimating the proportion of carbonic oxide necessary to make a confined atmosphere fatally poisonous, the time during which the gas is inspired is an important factor, and it is probable that the quantity required is much smaller than has hitherto been supposed, provided that respiration of the mixture is continued for several hours. C. H. B.

The Influence of certain Sulphur Compounds on Metabolism. By W. J. Smith (*Zeit. physiol. Chem.*, **17**, 459—467).—In a previous communication (*Therap. Monatsh.*, November, 1888), it

was shown that by metabolic changes sulphonal is converted into ethylsulphonic acid, whilst sulphuric acid is not formed in appreciable quantities. The present research relates to other sulphur compounds, and the experiments were carried out on a dog. For three days the animal received 1 lb. of dog biscuit and 1 litre of water daily. This was followed by a period of three days in which the drug was given in addition. The urine in the two periods was collected, analysed, and compared.

Acetone Ethylmercaptol.—There is no increase in the total sulphuric acid excreted, but qualitative examination showed the presence of an organic sulphur compound, which is readily soluble in water. Considering the near relationship of the drug given to sulphonal, it is probable that this compound is ethylsulphonic acid. The urine also contains small quantities of sulphonal.

α-Trithioaldehyde, $C_6H_{12}S_3$.—This is well absorbed from the intestine. The urine contains a small quantity of a sulphonate containing 39·3 per cent. of sulphur. Analysis of its crystals (m. p. 230°) agrees with the formula $C_6H_{12}S_3O_4$. The greater part of the sulphur appears in the urine as sulphuric acid.

Thioglycollic acid.—This causes sickness, but a small amount is absorbed, and leads to an increase in the urinary sulphates.

Ethylidenediethylsulphone.—There is a very slight rise in the urinary sulphates, and a small quantity of the drug was recovered unchanged from the urine.

Ethylenediethylsulphone.—There was no rise in the urinary sulphates.

The general conclusion drawn is, that urinary sulphates do not normally originate by oxidation of the sulphur-containing radicles in proteïd matter, but by oxidation of sulphur compounds analogous to thioglycollic acid, cystin, and cysteïn. W. D. H.

Phosphorus and the Lecithins. By W. Maxwell (*Amer. Chem. J.*, **15**, 185—195).—It has been shown in previous papers (Abstr., 1891, 489 and 511) that during the germination of seeds, the ratio of inorganic to organic phosphorus, presumably in the forms of phosphates and lecithins respectively, gradually decreases, the increase of the organic corresponding with the decrease of the inorganic phosphorus. It is now shown that during the development of the hen's egg, the ratio of inorganic to organic phosphorus gradually increases, the organic phosphorus, presumably in the form of lecithins, being converted into the phosphates of the bone of the chick. The lecithins were extracted from the yolk by alcohol and ether in succession, and the phosphorus of the extract converted into phosphate and weighed as magnesium pyrophosphate. The amount of phosphorus present in the form of nucleïns, and in the shell, is so minute as to be negligible. At a certain stage in the development, the organic phosphorus was observed to increase for a time, a phenomenon which may be attributed to the conversion of the original inorganic phosphates of the egg into lecithins by the organism, previously to reconversion into bone phosphates.

Jn. W.

Alkaloïds in Cod Liver Oil. By J. Bouillot (*Compt. rend.*, **116**, 439—441).—The alkaloïds of cod liver oil are of biliary origin, and pre-exist in normal hepatic tissue; they are not produced by any process of fermentation. If a thin section of the fresh tissue is exposed to gaseous hydrogen fluoride or hydrogen chloride for half an hour, and then dried under a bell-jar, numerous crystals can be observed under the microscope. These crystals are never enclosed in the hepatic cellules, but are localised in the extracellular liquid and in the biliary canaliculi; the hydrochlorides of dihydrotoluidine, aselline, and morrhuine can readily be recognised. If the section is moistened with a solution of platinic chloride, and again dried, the acicular crystals of morrhuine platinochloride are formed.

The author uses the term *pangaduine* to denote the mixture of all the alkaloïds contained in the oil. This mixture is soluble in alcohol of 80°, in an aqueous solution of glycerol, &c.; it leaves 3·5 per cent. of ash.

Pangaduine is of special value in all maladies characterised by imperfect nutrition: gout, rheumatism, diabetes, neurasthenic weakness, overwork, and all cases where there is abnormal production or elimination of toxines. In tuberculosis, pangaduine stimulates general nutrition, and thus increases the powers of resistance. C. H. B.

Excretion of Ethereal Hydrogen Sulphates in Cholera. By E. Baumann (*Zeit. physiol. Chem.*, **17**, 511—512).—Pouchet states that the excretion of ethereal sulphates in cholera is at a minimum. Renewed investigation of this point is necessary, taking into account the different stages of the disease. In some stages, the urine certainly contains excess of indican, and in pure cultures of the *Comma bacillus* indole is produced. W. D. H.

A Crystalline Globulin occurring in Human Urine. By D. Noël Paton (*Proc. Roy. Soc. Edin.*, **19**, 102—115).—In the urine of a patient recovering from a prolonged attack of diarrhœa, the percentage of proteïds was found to be very high—2·00 per cent., of which 1·92 consisted of globulin. On another occasion, the total proteïds were 3·82, of which globulin was 3·732. It was obtained by precipitation with ammonium sulphate, filtering, washing, and dialysing; the crystals were elongated and rhombic, and larger than those of tyrosine, but, instead of being acicular, they were terminated by a characteristic angular extremity—coagulation occurs below 60° and above 56°—dried at 110°, they were found to consist of C 51·89 per cent., H 6·88, N 16·06, S 1·24, O 23·93.

The remainder of the paper is of physiological interest only.

E. W. P.

Chemistry of Vegetable Physiology and Agriculture.

Ammoniacal Fermentation in Soils. By A. MÜNTZ and H. COUDON (*Compt. rend.*, **116**, 395).—When soil is sterilised by heating at 120°, ammoniacal fermentation is completely prevented. A temperature of 110° is not sufficient to produce this result. The production of ammonia is not due to a single organism, but several bacilli and micrococci, and some moulds, seem to be almost equally effective. It is noteworthy that nitrification, which is beneficial, is brought about by only one organism, whilst ammoniacal fermentation, which as a rule is harmful, can be produced by a comparatively large number of organisms. C. H. B.

The Nitrogen Question. By A. PETERMANN (*Bull. Acad. roy. Belg.* [3], **25**, 267—276; compare Abstr., 1890, 816, and this vol., ii, 33).—The object of the experiments described in this paper was to ascertain the effect of sterilisation on nitrogen fixation. The apparatus, of which a sketch is given, consisted of a large inverted bell jar (125 litres capacity) in which two flower pots were placed. The bell-jar was connected with an aspirator. The air before entering the bell-jar passed through cotton wool, and through vessels containing sulphuric acid, and sodium carbonate respectively. There was also an arrangement for boiling the water used for watering. The soil with mineral manure (the same as was used previously, *loc. cit.*) was sterilised by heating for five hours at 150°. The seeds were sterilised by immersion in mercuric chloride solution. The experiments were as follows:—(1) Soil, not sterilised, without higher vegetation, but covered with green and red algæ. (2) Sterilised soil, without vegetation of any kind. (3) Sterilised soil with barley. (4) Soil, not sterilised, with barley (this experiment was lost). (5) Sterilised soil, watered with sterilised water; no cryptogamic vegetation. (6) Soil, not sterilised, watered with rain-water; the soil gradually became covered with lower vegetation.

The numerical results, as regards nitrogen, are next given.

Nitrogen (grams).

	At commencement.			At conclusion.			Gain or loss.
	In soil.	In seed.	Total.	In soil.	In produce.	Total.	
1....	0·0255	—	0·0255	0·0294	—	0·0294	+0·0039
2....	0·0255	—	0·0255	0·0240	—	0·0240	−0·0015
3....	0·0511	0·0573	0·1084	0·0492	0·0575	0·1067	−0·0017
5....	0·0438	—	0·0438	0·0430	—	0·0430	−0·0008
6....	0·0438	—	0·0738*	0·0522	—	0·0769†	+0·0031

* Including 0·0300 gram in rain water added.
† Including 0·0247 gram in drainage.

The results show that barley is not able to fix free nitrogen, and that (as was always maintained by Schloesing) perfectly bare soils are also unable to fix nitrogen. Soils covered with lower vegetation become richer in nitrogen. This explains the previous results with barley (*loc. cit.*); the gain of nitrogen in these experiments was not due, as was then supposed, to fixation by the barley itself, but was brought about by the algæ with which the surface of the sand was more or less covered. Both the earlier, and the new, results are thus in accordance with those of Hellriegel and Wilfarth, and of Schloesing, jun., and Laurent, in showing nitrogen fixation by leguminous plants in symbiosis with nodule organisms, and by lower vegetation, and the absence of such fixation in the case of sterilised soils, and in a non-leguminous higher plant alone. N. H. M.

Pre-existence of Gluten in Wheat. By BALLAND (*Compt. rend.*, **116**, 202—204).—According to Johannsen, no gluten can be obtained from wheat by washing with water at 0°, but the quantity increases with the temperature up to 40°, and then diminishes as the temperature rises. The author finds, however, that gluten can be obtained by treating wheat flour that had been kept for several days at −8° with water at 2°; and experiments made at 2°, 15°, and 60° with the same flour gave respectively 27·0, 27·6, and 30 per cent. of moist gluten. If flour is kept for 36 hours in an atmosphere containing sulphurous anhydride produced by the combustion of 60 grams of sulphur per cubic metre, no gluten can be obtained by the usual method, but it can readily be separated by using water containing salt in solution, or by mixing the flour with a known weight of moist, well-washed gluten, and proceeding in the usual manner.

The author concludes that gluten pre-exists in wheat.

C. H. B.

Proteïds of Linseed. By T. B. OSBORNE (*Amer. Chem. J.*, **14**, 629—661).—The paper contains a detailed account of the manner in which the proteïds were separated: for this the original must be consulted. The main results of the experiments were as follows:—Extracts of linseed meal (with water, aqueous sodium chloride, and dilute aqueous potash) contain a globulin precipitable by dialysis; a proteïd, resembling both globulin and albumin, precipitable by long-continued heating at 100°, as well as by sodium chloride in the presence of an acid; proteose and peptone-like substances, and a proteïd not extracted by sodium chloride solution, but soluble in dilute aqueous potash. All attempts to determine the amounts of these various substances failed because of change, while in solution, into non-proteïds. It was further found that the relative amount of the various proteïds was very variable; it is almost certain that the more soluble forms were largely, if not wholly, derived from the globulin in consequence of alteration during extraction and separation. The globulin crystallised in octahedral crystals or in spheroïds, and in composition is similar to the globulin of squash seed. It has a tendency to become partially transformed into an "albuminate," which is insoluble in cold sodium chloride solution, but dissolves in dilute sodium carbonate, and also in warm sodium chloride, being reconverted in the last

case into the original globulin. A proteose was obtained resembling closely in composition the deuterovitellose formed when the crystallised vitellin of squash seeds is digested with pepsin-hydrochloric acid.

C. F. B.

Analyses of Kale and Turnip Salad, and Okra. By J. D. TINSLEY (*Amer. Chem. J.*, **14**, 625—626).—The kale and okra pods were weighed immediately after cutting, the turnip salad not until after some hours, when it had wilted somewhat.

100 parts of the "fresh" plant.	Kale salad.	Turnip salad.	Okra pods.
Water by air-drying	88·34	77·78	83·07
Water at 100°	1·32	2·27	1·64
Solid matter	10·34	19·95	15·29
Solid matter containing—			
Pure ash	1·22	2·62	0·91
Ether extract	0·65	1·59	0·29
Crude fibre	1·15	1·57	1·44
Crude starch, gum, &c.	3·43	8·07	10·12
Crude protein	3·89	6·10	2·53
Nitrogen, total	0·62	1·12	0·41
Nitrogen, proteïd	0·25	0·68	0·28

C. F. B.

Analyses of "Black Earth." By F. P. DUNNINGTON and T. C. WHITLOCK (*Amer. Chem. J.*, **14**, 621—623).—The following two analyses are given, one (I) of a soil from the prairie land of Red River, near Winnipeg, Manitoba, the other (II) of Russian tschernozem or black earth from District Balashoff, Government of Saratoff; the two soils are similar in appearance.

	Sand.	Amorph. SiO_2.	Fe_2O_3.	Al_2O_3.	TiO_2.	CaO.	MgO.	SO_3.	CO_2.
I.	59·82	5·45	4·00	7·14	0·64	0·61	0·61	0·03	0·37
II.	53·71	12·80	4·13	6·04	0·63	0·75	0·21	0·06	0·02

	P_2O_5.	K_2O.	Organic matter*.	H_2O.	Total.
I.	0·13	1·91	12·49	6·86	99·76
II.	0·16	1·97	14·91	5·04	100·43

The two soils are thus similar in chemical composition; they occur in the same latitude, with the same general relief and climate, and have a similar geological history. "May they not therefore be properly considered as of the one variety of soil, 'black earth?'"

C. F. B.

* Contains humus, 0·45 and 0·44, and total nitrogen, 0·44 and 0·31 respectively.

Analytical Chemistry.

Use of Thallium Silver Nitrate for Separating Minerals. By J. W. Retgers (*Jahrb. f. Min.*, 1893, i, Mem. 90—94).—In an investigation of the isomorphous relations between silver nitrate and the alkali nitrates, the author observed that the double salts of silver nitrate with potassium and ammonium nitrates had very low melting points in comparison with the simple salts. The lowering of the melting point is still more considerable in the case of the thallium double salt, as is shown by the following figures.

	$TlNO_3$.	$AgNO_3$.	$TlAgN_2O_6$.
Melting point.....	205°	224°	75°

The remarkable fusibility of this salt, together with its high specific gravity, suggested the possibility of employing it in a molten condition for separating minerals. The results have been found to be thoroughly satisfactory. The sp. gr. of the molten mass is about 5·0, for zircon (sp. gr. 4·5) and braunite (sp. gr. 4·8) float, whilst magnetite (sp. gr. 5·2) sinks. The salt may easily be fused over a water-bath, the result being a colourless, limpid liquid. With this salt, the author has been able to separate from the sand of the Dutch coast a large number of garnets, some zircon crystals, rutile, and magnetite grains. B. H. B.

Estimation of Precipitates by an Optical Method. By E. Aglot (*Compt. rend.*, **116**, 200—202).—The quantity of precipitate is determined by measuring the length of the column of turbid liquid necessary to cut off the visible form of the brightest part of a flame such as that of a petroleum lamp. The apparatus used is of the same type as a Dubosq colorimeter. In order to keep the precipitate in suspension and secure homogeneity, the liquid is mixed with gum, dextrin, glucose, &c. Constants have, in the first place, to be determined for each substance in various degrees of concentration, and also for each observer. C. H. B.

Normal Borax Solution. By T. Salzer (*Ber.*, **26**, 430; compare Rimbach, this vol., ii, 233).—A question of priority.

Sensitive Litmus Indicator. By J. Lüttke (*Zeit. anal. Chem.*, **31**, 692).—100 grams of litmus is extracted with warm water, and the extract, concentrated to 200 c.c., is mixed with 20 c.c. of 25 per cent. hydrochloric acid, and dialysed until the acid is removed. The residual colour is extremely sensitive to traces of acid or alkali. By precipitating the concentrated solution with alcohol and drying the precipitate, a solid preparation is obtained which can be kept unchanged for a long time. Another method consists in spreading the solution on glass plates and drying in a stream of carbonic anhydride. M. J. S.

Quantitative Spectrum Analysis. By G. KRÜSS and H. KRÜSS (*Zeit. anorg. Chem.*, **1**, 104—125).—This paper contains many useful practical details. It is divided into three sections:—1. *Comparison of Various Methods of Quantitative Spectrum Analysis.* 2. *Influence of Temperature on the Absorption Spectrum of Coloured Solutions.* 3. *Improved Form of Vierordt's Spectrophotometer.* A drawing is given of the apparatus described in the third section. A. R. L.

New Direct Separation of Chlorine, Bromine, and Iodine. By P. JANNASCH and K. ASCHOFF (*Zeit. anorg. Chem.* **1**, 144—149 and 245—247).—The authors proceed at first on the same lines as Gooch (Abstr., 1891, 361), thus:—A solution of sodium chloride, potassium bromide, and potassium iodide (about 3 grams of each) is dissolved in water (750 c.c.), acidified with dilute sulphuric acid (*loc. cit.*), and a solution of sodium nitrite (1 gram) in water (10 c.c.) added. Instead of boiling off the iodine and allowing it to escape, a current of steam is passed through the mixture, contained in a specially constructed flask, whereby the liberated iodine is driven off in a quarter of an hour, and is collected as iodide in a second flask containing a mixture of 5 per cent. sodium hydroxide solution (50 c.c.) and 3 per cent. hydrogen peroxide (50 c.c.).

The residual mixture of chloride and bromide is now rendered alkaline, evaporated to about 50 c.c., acidified with dilute (1 : 3) acetic acid (60 c.c.), and a concentrated solution of potassium permanganate (1—1·5 grams) added. A slow current of steam is then passed through, whereby all the bromine (but no chlorine) is driven over in 45 minutes, and may be collected in sodium hydroxide solution. The residual solution containing the chloride is treated with soda and alcohol, and the precipitated manganese oxide filtered off and washed; the three halogens can now be precipitated separately with silver nitrate as usual.

In the second communication, the authors state that when chemically pure acetic acid is employed with their method, the values obtained for bromine are no longer low. A brisk current of steam is passed through the solution containing chlorine and bromine during the distillation, in order to drive over the bromine as quickly as possible; the distillation lasts 1¼ hours. The manganese is precipitated from the residual liquid by ammonia and hydrogen peroxide, the precipitate collected and washed with 1 per cent. sodium nitrate solution before determining the chlorine in the filtrate.

A. R. L.

Microchemical Detection of Sulphur. By F. EMICH (*Zeit. anal. Chem.*, **32**, 163—167).—With scarcely an exception, metallic sulphides, when reduced to fine powder, moistened with a solution of calcium chloride, and exposed for a few minutes to the vapours from saturated bromine water, undergo oxidation, resulting in the formation of calcium sulphate, the characteristic crystals of which can be identified by microscopic examination. With a magnifying power of 300 diameters, as little as 0·00002 milligram of sulphur affords distinct indications. Out of 59 mineral sulphides examined, molybdenite alone resisted oxidation obstinately, 20 hours elapsing before

any calcium sulphate crystals could be observed; a momentary roasting, however, accelerated the operation immensely.

For organic sulphur compounds, the reaction is not a general one, although it succeeds with some, such as the thiocyanates, thiourea, mustard seed, and the mustard oils, &c. M. J. S.

Estimation of Nitrogen in Coal Gas. By C. H. New (*J. Soc. Chem. Ind.*, **11**, 415—418).—The method consists in first removing the majority of the bases and certain hydrocarbons, such as benzene and xylene, by passing the gas through concentrated sulphuric acid (sp. gr. 1·85), and then converting the whole of the remaining hydrocarbons into carbonic anhydride and water, by conducting the gas over red-hot copper oxide. The gases which result from this treatment consist of carbonic anhydride and nitrogen, so that the former may be absorbed by soda, and the volume of the remaining nitrogen ascertained.

The apparatus employed consists of the following parts:—1. An apparatus for generating carbonic anhydride. 2. A burette graduated to hold 100 c.c. of gas, fitted at the top with a three-way tap, and connected at its lower extremity with an aspirator. 3. A combustion furnace, containing a combustion tube about 80 cm. long, projecting some 10—12 cm. beyond the furnace, and packed with coarse copper oxide to within 7 cm. of the ends of the tube, which are fitted with india-rubber corks; through each of these a piece of small-bore glass tubing passes, one of these being connected with a small bottle of about 30 c.c. capacity, containing concentrated sulphuric acid. 4. A receptacle for collecting the carbonic anhydride and nitrogen resulting from the combustion of the coal gas, capable of holding 200 c.c., and graduated with a containing mark at 150 c.c. and at 200 c.c. 5. A Hempel's gas apparatus.

The method, which may be carried out in 30 minutes, consists in raising the combustion tube and its contents to a full red heat, during which operation a current of air is aspirated through the tube. The air is then stopped, and a brisk current of carbonic anhydride passed through the sulphuric acid absorber and combustion tube, the generating apparatus having been attached to the latter through the three-way tap. The tube connecting the three-way tap with the absorbing bottle is now closed by a pinch-cock, and the gas receiver, having been filled completely with mercury, is connected with the other end of the combustion tube, taking care to avoid the entrance of any air. The pinch-cock intervening between the carbonic anhydride generator and the three-way tap is also closed. The india-rubber tube connecting the absorption bottle with the three-way cock is then temporarily removed, and after displacing all air in the burette with mercury, coal gas is admitted by connecting with the gas supply and lowering the aspirator bottle, the gas being adjusted to the 100 c.c. mark by levelling the height of the mercury. The absorption bottle is now again connected with the three-way tap, and the pinch-cocks both here and at the top of the receiver are opened. The gas is then slowly chased over from the burette through the absorption bottle and the combustion tube, the rate at which the gas is passing being

ascertained by observing the bubbles in the absorber. The displacement of the 100 c.c. of gas should occupy about 15 minutes. The connection with the burette is then closed, and the tap once more connected with the carbonic anhydride generator, from which a current of gas is slowly passed through the whole apparatus, displacing the coal gas in the absorber, and carrying over all the nitrogen in the combustion tube into the receiver. The mercury in the receiver is brought nearly to a level during the experiment, maintaining the gas, however, under a slight pressure, and adjusting the same by means of the small tap at the bottom, so that when the gas reaches the 150 c.c. mark, and the pinch-cock at the top and the tap at the bottom are simultaneously closed, the levels of the two columns of mercury are coincident with each other. The receiver is then disconnected, and the combustion tube having been opened to the air, the pump is again started to reoxidise the copper oxide. The wide mouthed limb of the receiver is then filled with mercury, and 100 c.c. of the gas passed into the Hempel burette, the carbonic anhydride being absorbed with soda in the usual way. It has also been found necessary to remove traces of oxygen from the gas before taking the final reading of the nitrogen. The volume of the remaining gas is then noted, calculated to 150 c.c., and after correction for temperature and pressure gives the volume per cent. of nitrogen. D. B.

Dumas' Method of estimating Nitrogen in Organic Substances. By J. O'SULLIVAN (*J. Soc. Chem. Ind.*, **11**, 327—328).—The author's experience with the absolute method of Dumas proves that the gas obtained invariably contains an appreciable quantity of nitric oxide, and that the amount is not much influenced by the presence of the usual copper in the combustion tube. By discarding the copper, and substituting a plug of asbestos, not much more nitric oxide is found in the gas. This does away with the tedious process of reducing the oxidised copper. As there is always nitric oxide in the gas, more accurate results are obtained by measuring the quantity of nitric oxide and nitrogen by means of a gas analysis apparatus.

D. B.

Stock's Process for the Estimation of Nitrogen. By W. F. K. STOCK (*Analyst*, **18**, 58, and 58—60).—The author (compare Abstr., 1892, 1592) has dispensed with one of the bunsen burners. The apparatus has been simplified, and now consists of a 150 c.c. Wurtz flask, the tube of which runs into the condenser, and is kept at boiling point by the ammoniacal steam from the distilling flask. Not a trace of sodium hydroxide finds its way into the distillate.

The author, in the second paper, defends his process against an attack made on it by Skertchly, who does not seem to have strictly followed the directions given. L. DE K.

Estimation of Nitric acid by means of Cinchonamine Salts. By P. GAMMARELLI (*Gazzetta*, **22**, ii, 635—642).—Arnaud's method of estimating nitric acid (Abstr., 1884, 87), based on the sparing solubility of cinchonamine nitrate, is of little value. 100 parts of a

saturated aqueous solution contain 0·21 part of the salt at 11·5°, so that a loss of 3 per cent. or so is incurred, even when the minimum quantity of liquid is employed in the analysis. The solubility of the salt remains practically the same when a 1 per cent. aqueous solution of potassium sulphate or chloride is used in place of water. The *nitrite* forms small prisms, which melt at 174° with decomposition; it is more soluble than the nitrate, 100 parts of its saturated aqueous solution containing 0·52 part of the salt at 10·4° and 0·63 part at 13·8°. W. J. P.

Reaction of Nitrites, and its Applications. By C. M. Van Deventer (*Ber.*, **26**, 589—593).—Schäffer pointed out long ago that an intensely yellow liquid is obtained when a few drops of potassium ferrocyanide and then a little acetic acid are added to a very dilute sulphuric acid solution of potassium nitrite. The author finds that the action in this case is expressed by the equation $2K_4Fe(CN)_6 + 2HNO_2 + 2C_2H_4O_2 = K_6Fe_2(CN)_{12} + 2KC_2H_3O_2 + 2NO + 2H_2O$, and that even in the cold the formation of nitric oxide takes place quantitatively, so that the reaction can be made use of not only for the preparation of nitric oxide, but also for the detection and estimation of nitrous acid.

For preparing nitric oxide, a mixture of solutions of potassium ferrocyanide and potassium nitrite is gradually added from a stoppered funnel to a flask containing acetic acid; the contents of the flask must be vigorously shaken during the operation.

Nitrous acid can be detected, even in presence of nitric acid, which is without influence, by the evolution of nitric oxide which takes place on mixing the above-mentioned solutions, provided that the quantity of nitrite is not so small that the whole of the gas remains in solution; a feeble, and only a momentary, gas evolution is observed when about 4 milligrams of potassium nitrite are present in every 20 c.c. of the mixture of the three solutions.

The estimation of nitrous acid can be conveniently carried out as follows. A eudiometer, provided with a stopcock, is completely filled with an approximately 14 per cent. solution of potassium ferrocyanide, and the open end is then dipped vertically into a vessel containing the same liquid; the nitrite solution is introduced with the aid of a funnel attached to the upper end, the funnel being washed first with a little water, then with acetic acid, and finally with a small quantity of concentrated potassium ferrocyanide. As soon as the gas evolution begins to slacken, the eudiometer is vigorously shaken, the open end being kept dipped into the solution of potassium ferrocyanide, until the level of the liquid in the eudiometer remains stationary. Water is then slowly introduced at the top with the aid of a funnel, and, as soon as the potassium ferrocyanide solution has been almost completely displaced, the open end is closed with the thumb and the tube vigorously shaken; it is then dipped into the potassium ferrocyanide solution, and, after some time, the volume of the nitric oxide is observed. The usual corrections are made for temperature and pressure, and also for the quantity of gas which has been dissolved by the water in the apparatus. Quantitative

experiments gave results agreeing with one another, and also with those obtained by Péan de St. Gilles' method, so that, in case standard solutions are not at hand, the direct measurement of the gas in the manner described may be recommended as a convenient method for the estimation of nitrous acid. F. S. K.

Spica's Process for the Estimation of Phosphoric acid. By C. Arnold and K. Wedemeyer (*Zeit. angw. Chem.*, 1892, 603—604).—Spica estimates the amount of phosphoric acid in basic slags by heating them with strong sulphuric acid, and then extracting the mass with a large quantity of absolute alcohol to dissolve the phosphoric acid. After the alcohol has been expelled, the liquid is neutralised and titrated with a standard solution of potassium ferric sulphate with salicylic acid as indicator. The authors have investigated the process, but cannot recommend it. A sample which gave 17·88 per cent. of phosphoric acid by the molybdate process only gave 16·59 per cent. by titration. L. de K.

Separation and Estimation of Pyrophosphoric and Meta-phosphoric acids. By G. v. Knorre (*Zeit. angw. Chem.*, 1892, 639—641).—Estimation of Pyrophosphoric acid.—Acid sodium pyrophosphate ($Na_2H_2P_2O_7 + 6H_2O$) is neutral towards methyl-orange and tropæolin. If, therefore, hydrochloric acid is added to a solution of normal sodium pyrophosphate ($Na_4P_2O_7 + 10H_2O$), the end reaction will only make its appearance when all the normal pyrophosphate has changed into the acid salt. The test analyses are satisfactory.

A solution of normal sodium pyrophosphate is strongly alkaline towards phenolphthaleïn. If, therefore, a solution of the acid phosphate is titrated with potash, the results will be too low, as the end reaction already shows long before the acid salt has become neutralised. The author has, however, succeeded in getting good results by titrating with lime-water in presence of calcium chloride, which precipitates the normal salt and so removes the alkalinity. If a solution contains both acid and normal pyrophosphates, the latter may be estimated by means of methyl-orange and standard acid. The total amount of phosphate may then be determined by means of calcium chloride and standard lime-water with phenolphthaleïn as indicator.

To detect pyrophosphoric acid in presence of the meta-acid, the author recommends the addition of zinc acetate to the perfectly cold solution, which will precipitate the least trace of the pyro-compound; but attempts to render this a means of quantitative estimation proved unsuccessful. L. de K.

Estimation of Arsenic. By H. Bäckström (*Zeit. anal. Chem.*, 31, 663—665).—The author advocates the weighing of arsenic as pentoxide after precipitation as sulphide. The solution containing the arsenic is treated with hydrogen sulphide, first at the ordinary temperature and then on the water bath. It is immaterial whether the precipitate is trisulphide or pentasulphide, or contains free sulphur. After complete washing, it is rinsed from the filter into a beaker, any particles adhering to the filter being dissolved by am-

monia. After drying on the water bath, it is oxidised by repeated careful additions of rectified fuming nitric acid in small portions. When the sulphur is wholly oxidised, the liquid is transferred to a platinum crucible, and, after evaporation, is heated to a temperature just short of redness to expel sulphuric acid, the last traces of which are somewhat stubbornly retained. Complete deprivation can, however, be attained without decomposition of the arsenic pentoxide, which is stable at temperatures below a red heat. Being hygroscopic, it must be weighed with rapidity. The results are as accurate as can be desired. M. J. S.

Estimation of Silica in Clay. By L. Archbutt (*J. Soc. Chem. Ind.*, **11**, 215—217).—Craig (Abstr., 1890, 194) states that by fusing pure silica or siliceous material with alkali carbonates, not more than 97·5 per cent. of the silica can be found in the insoluble residue, and this statement has led Gilbert (Abstr., 1890, 1026) to make a number of experiments, which show that in the analysis of silicates containing alumina, but practically free from lime and magnesia, dehydration, even at 280°, will not prevent some milligrams of the silica from passing into the filtrate, so that in accurate analyses the silica in the filtrate must always be recovered. From the author's experiments, it appears almost hopeless to obtain by a single dehydration the whole of the silica, and the following process has been adopted as being more trustworthy. 1 gram of the finely-powdered clay is fused with 5 grams of pure, mixed alkali carbonates. The mass is extracted with about 200 c.c. of water, the solution acidified with hydrochloric acid in good excess, and evaporated to dryness on the steam bath in a porcelain dish, reducing the residue to small grains. It is then heated in an air oven at 150° for one hour, dissolved in hydrochloric acid and water, filtered, and the silica washed. The filtrate is evaporated with 20 c.c. of strong sulphuric acid until fumes are evolved very strongly. The residue is then dissolved in hydrochloric acid and water, and the additional small quantity of silica collected and washed. The mixed residues are ignited at the highest temperature of the muffle until constant in weight. The silica is then volatilised with hydrofluoric acid and a few drops of sulphuric acid, and the residue ignited until constant in weight. The difference is pure silica. D. B.

Estimation of Potassium. By E. W. Hilgard (*Zeit. anal. Chem.*, **32**, 184—185).—The platinochloride is decomposed by ignition in a platinum crucible, the lower half of whose inner surface has previously been covered with a layer of platinum sponge by strong ignition of some of the double salt. The presence of the sponge greatly facilitates the decomposition at even a moderately low temperature. When decomposition is complete, the crucible is strongly ignited for some time. This consolidates the reduced platinum, thus preventing loss when washing out the soluble matters. A little hydrochloric acid is then warmed in the crucible, and if it acquires a yellow colour, the ignition is repeated with the addition of oxalic acid. The soluble matters are then washed out with acidified boiling water, and the residual

platinum is weighed. Since the washing usually removes some sodium chloride and traces of earths, together with silicates, from the filter ash, the results are lower and more accurate than those from weighing the double salt. M. J. S.

Detection of Ammonia with Nessler's Reagent. By L. L. DE KONINCK (*Zeit. anal. Chem.*, **32**, 188).—An alcoholic solution of ammonia gives neither precipitate nor coloration with Nessler's reagent. Alcohol does not, however, hinder the reaction of ammonia with mercuric chloride (Bohlig's test). M. J. S.

Separation of Strontium from Calcium. By R. FRESENIUS (*Zeit. anal. Chem.*, **32**, 189—203).—Rose's method of digesting the sulphates with a strong solution of ammonium sulphate, Fleischer's method of boiling the oxalates with potassium sulphate, and Sidersky's methods of precipitation with a mixture of ammonium sulphate and oxalate are all subject to the same defect of affording only approximately correct numbers as the result of compensating errors. In all cases each of the separated constituents is found to be largely contaminated with the other. Stromeyer's method, as improved by Rose, which consists in the treatment of the anhydrous nitrates with a mixture of equal volumes of absolute alcohol and ether, affords an almost perfect separation. When very carefully dried at 130°, 1 part of strontium nitrate requires 83,044 parts of the ether alcohol for solution, whilst 1 part of calcium nitrate dissolves in 1·87 parts. The following mode of conducting the separation yields excellent results. The nitrate solution is evaporated in a small porcelain basin and dried for a long time at 130°. The residue is rubbed to powder and rapidly treated, with rubbing, five times with 5 c.c. of the ether alcohol, pouring the solution into a small flask. The residue in the basin is dissolved in water, re-evaporated, and dried at 130°, rubbed to powder, and transferred as completely as possible to the flask, the basin being thrice rinsed with 5 c.c. of the ether alcohol. The flask is then frequently shaken during 24 hours, and the solution of the calcium nitrate filtered through a small filter, washing the residual strontium nitrate and the filter by 12 decantations with 5 c.c. of ether alcohol each time. In a separation reported, the strontium came out 0·17 per cent. too high, and the calcium 0·56 per cent. too low, and spectral analysis showed only traces of each metal in the precipitate of the other. M. J. S.

Volumetric Determination of Calcium Phosphate by means of Uranium Solution. By J. B. COLEMAN and J. D. GRANGER (*J. Soc. Chem. Ind.*, **11**, 328—329).—It is stated by some authorities that in estimating calcium phosphate by means of uranium solution, correct results are only obtainable when the solution is standardised with calcium phosphate in the place of sodium phosphate. This statement is confirmed by the authors, who found the results were otherwise low, especially in cases where the proportion of calcium phosphate was considerable. It is also necessary to estimate the percentage of

phosphoric acid in the calcium phosphate used for standardising by the gravimetric method. D. B.

Volumetric Estimation of Lead. By F. C. KNIGHT (*Chem. News*, **67**, 128—129).—The author, having satisfied himself that lead oxalate is practically insoluble under the conditions involved, has adopted the following method for estimating lead for technical purposes. The lead (0·05—0·5 gram), if necessary, having been reduced to the metallic state, is dissolved in 3 c.c. of concentrated nitric acid, diluted with 10 c.c. of hot water, and precipitated with slight excess of sodium carbonate. The precipitate is dissolved in 5 c.c. of strong acetic acid, the solution mixed with 20 c.c. of 95 per cent. alcohol, heated to 65°, and the lead precipitated by adding 10 c.c. of a saturated solution of oxalic acid. This precipitate, after washing thoroughly with hot water, is placed in a beaker with 50 c.c. of hot water, and 5 c.c. of concentrated sulphuric acid is added. The solution is warmed to 65°, and the liberated oxalic acid titrated with standardised permanganate. D. A. L.

Estimation of Oxygen in Lead. By G. LUNGE and E. SCHMID (*Zeit. anorg. Chem.*, **2**, 451—460).—The authors find that lead usually contains but a very minute trace of oxygen, about 0·0025 per cent., but that when the lead is contaminated with from 0·01 to 1 per cent. of copper the quantity of oxygen is much increased. A special form of apparatus was employed for passing hydrogen over the heated lead and absorbing the water formed. G. T. M.

Gravimetric Estimation of Zinc as Sulphide. By W. F. LOWE (*J. Soc. Chem. Ind.*, **11**, 131—133).—The usual method of estimating zinc in blende and other ores of zinc by a standard solution of sodium sulphide, although fairly rapid and sufficiently accurate for many purposes, cannot be considered a very satisfactory process. The gravimetric method is very little used, owing to the supposed difficulty of filtering zinc sulphide; but if the necessary precautions are taken, very little difficulty will be experienced and very accurate results obtained. 1 gram of the dried and finely-ground sample is placed in a conical flask, 10—15 c.c. of strong hydrochloric acid added, the flask covered with a small funnel, and boiled on an iron plate until dissolved. Two or three drops of strong nitric acid are then added to ensure the complete solution of the ore. This addition should not, however, be made until the solvent action of the hydrochloric acid is complete, as otherwise a separation of sulphur takes place. As soon as all the nitrous fumes have passed off, the solution is diluted to about 100 c.c. with cold water, and a good stream of hydrogen sulphide passed through until the precipitate turns black and settles readily. It is then filtered through a covered filter, and washed with water containing a little hydrogen sulphide. The solution is then heated in an uncovered beaker on the iron plate to a temperature just below boiling. As soon as the hydrogen sulphide has passed off, some bromine water is added to oxidise the iron, the solution cooled, and an excess of ammonia is added. It is allowed to stand for a few minutes on the iron plate, and filtered.

The precipitate is washed slightly, and is then redissolved in warm hydrochloric acid, reprecipitated with ammonia, filtered through the same paper, and washed with hot water containing a little ammonia. The solution is made up with hot water to about 750 c.c., and is heated in a conical flask nearly to boiling. About 10 c.c. of freshly-prepared, colourless ammonium sulphide is added, and the solution boiled for two or three minutes and allowed to settle. The boiling converts the slimy precipitate into a granular one. The flask is then covered and left to stand all night, the clear liquid is siphoned off to just above the precipitate, and this portion, although having only a slight opalescence, is filtered through a double filter of good Swedish filter-paper, and it is important that the filter should exactly fit the funnel, and be held down in its place whilst it is moistened before use. After the decanted portion has been filtered, the precipitate is washed once by decantation with hot water containing a little ammonium chloride and a few drops of ammonium sulphide. It is transferred with hot water, containing a few drops of ammonium sulphide, to the filter, which is kept covered with a ground glass plate. The precipitate is then dried, transferred to a Rose's crucible, the filter being burnt in a separate crucible, and the ash added to the precipitate, a little pure sulphur is added, and the whole ignited in a current of coal-gas, at first gently and then for about five minutes in a large Bunsen flame. After cooling in the current of coal-gas, it is weighed. The results quoted show the process to be very accurate.

If the ores contain manganese, the process requires to be modified; the zinc can be precipitated as sulphide in an acetic acid solution, or the manganese can first be removed by precipitation with bromine.

D. B.

Volumetric Estimation of Zinc. By B. C. Hinman (*Chem. News*, **67**, 30—32).—Preliminary experiments proved that Von Schulz and Low's method of determining zinc, whilst satisfactory for readily decomposable ores containing little or no iron, requires modification under other circumstances, inasmuch as the iron precipitate carries zinc down with it; manganic oxide, however, does not behave in this manner. The modified method is as follows:—The very finely-pulverised ore is treated with nitro-hydrochloric acid, either until decomposition is complete or until action ceases; if decomposition is then incomplete, the mass is taken to dryness, heated to dehydrate the silica, and then treated with dilute hydrochloric acid; the insoluble residue is fused with sodium carbonate and nitrate, dissolved in hydrochloric acid, and added to the other solution, which is now boiled with nitric acid until all the hydrochloric acid is expelled, then taken nearly to dryness, and, after the addition of the usual quantity of nitric acid, saturated with potassium chlorate, and evaporated to total dryness. The dry residue is treated with ammonium chloride and ammonia, the solution diluted, and heated to boiling; the precipitate is collected, washed with weak ammonium chloride rendered alkaline with ammonia, then dried, and re-treated with the chlorate mixture. The solutions are then mixed and acidified to the same degree as that employed when standardising; to effect this, a small

quantity of an indicator is added to the solution, and, after neutralising, the measured quantity of acid is run in. The acidified solution is heated to boiling, and titrated with ferrocyanide. D. A. L.

Separation of Iron from Aluminium. By H. Bornträger (*Zeit. anal. Chem.*, **32**, 187).—After weighing the ignited oxides, they are dissolved in hydrochloric acid, and potash (not soda) added until the solution is nearly neutral. The oxides are then precipitated hot by neutral potassium oleate, avoiding excess. The precipitate is washed on a filter with hot water, and after drying over calcium chloride until most of the water is removed, it is treated with hot petroleum, which dissolves the ferric oleate. The residual aluminium oleate is ignited, and leaves alumina as a porous, white mass. The filtrate can be evaporated and ignited in a platinum basin so as to weigh the ferric oxide. Ferrous oxide may be separated from alumina by the same treatment without oxidation. The results are very exact. M. J. S.

Estimation of Manganese in Iron. By M. A. v. Reis (*Zeit. angw. Chem.*, 1892, 604—607; 672—674).—Of the numerous processes recommended from time to time, the author prefers the following:—About 1 gram (or more) of the sample is dissolved in 25 c.c. of an acid mixture containing 275 vols. of water, 125 vols. of nitric acid (sp. gr. 1·4), and 100 vols. of strong sulphuric acid. The mixture is heated over a naked flame, and evaporated until sulphuric fumes escape. After cooling, the liquid is diluted to about 100 c.c. with water, another 10 c.c. of the acid is added, and the mixture heated until the salts have dissolved. To destroy any carbon, the solution is introduced into a 1 litre Erlenmeyer flask, and boiled for four minutes with 3 grams of barium peroxide and 5 c.c. of nitric acid. 400 c.c. of boiling water is next added, then a sufficiency of an emulsion of zinc oxide (20 grams of ZnO generally suffices), and the manganese may then at once be titrated with a standard solution of potassium permanganate.

From the author's test analyses, it appears that the accuracy of the process is not influenced by the amount of acid or zinc oxide used, provided these substances are free from manganese and not used in inordinately large quantities. L. de K.

Analysis of Ferrosilicon and Siliceous Spiegel. By T. W. Hogg (*Chem. News*, **67**, 27—28).—It is pointed out that the impression that high-percentage ferrosilicon and siliceous spiegel is very imperfectly attacked by nitrohydrochloric acid is a misconception, arising, firstly, from comparatively coarse particles becoming covered with a protective coating of silica, and, secondly, from the silica retaining iron oxide, which it takes up during the dry heating usually practised subsequent to the treatment with the acid. The first obstacle can be removed by grinding the portion of alloy intended for analysis to extreme fineness in an agate mortar, whilst the second may be avoided by filtering off the silica and graphite after the treatment with acid, and evaporating the filtrate to dryness by itself, in order to obtain the small quantity of dissolved silica. When titanic oxide is

present, and great accuracy is required, treatment with sulphuric and hydrofluoric acid would be adopted. D. A. L.

Decomposition of Tin Slags by the Fluoride Method. By H. N. WARREN (*Chem. News*, **67**, 16).—The following method is not only rapid, but also eliminates risk of loss by volatilisation. The pulverised slag is gently heated, for a few moments, on a sand-bath, in a platinum vessel, with a mixture of equal parts of hydrofluoric and hydrochloric acids; the solution is diluted to a known volume; half of it is precipitated with hydrogen sulphide, and the precipitated mixed sulphides of tin and antimony, after purification by redissolving, &c., if necessary, are ignited and weighed as oxides. The other half is rendered alkaline with ammonia, excess of oxalic acid is added, and by means of hydrogen sulphide the antimony sulphide is now precipitated alone, and is ignited and weighed. The percentage of tin is readily ascertained by deducting this weight from that of the mixed oxides. D. A. L.

Quantitative Analysis by Electrolysis. By F. RÜDORFF (*Zeit. angw. Chem.*, 1892, 695—698).—Estimation of *Gold*.—The author (compare this vol., pp. 93—95) dissolves a few grams of potassium cyanide in water contained in a platinum dish, the inside of which is coated with silver. The gold solution, which should contain no more than 0·3 gram of the metal, is now added, and the mixture is diluted to about 120 c.c. Two or three Meidinger cells are used, and the gold is deposited as a lustrous, smooth, adherent mass, which may afterwards be readily removed by warming with nitric acid.

Estimation of *Platinum*.—The solution should contain no more than 0·5 gram of the metal. After adding five drops of 10 per cent. sulphuric acid, and diluting to 120 c.c., the platinum is completely precipitated by electrolysing with two cells. If the basin is afterwards well rubbed with sand, the metal becomes smooth and lustrous, and the dish will have increased in value.

Separations: *Copper from Silver*.—The total amount of metal should not exceed 0·5 gram. If the amount of copper is about equal to or less than the silver, the neutralised solution is mixed with 8 grams of potassium cyanide, diluted to 120 c.c., and electrolysed with two or three cells. After 12 hours, the silver will have separated out completely, and is free from copper. The liquid is evaporated to dryness after the addition of sulphuric acid, the residue is dissolved in water, and mixed with 3 grams of ammonium nitrate and 20 c.c. of ammonia (sp. gr. 0·91). After diluting to 120 c.c., the solution is electrolysed by means of four or five cells, and the precipitated copper is treated as previously directed.

Copper from Mercury.—The solution should contain about 0·4 gram of metal. If the amount of copper is less than the mercury, 6 grams of potassium cyanide is added, the whole diluted to 120 c.c., and electrolysed with two or three cells. If, however, the copper preponderates, 10 grams of potassium cyanide should be added. The mercury separates within 12 hours, and the copper is afterwards estimated as directed.

Copper from Cadmium.—The author recommends dividing the solution into two parts, and precipitating the copper in the one, and the cadmium in the other. The solution, which should not contain more than 0·5 gram of metal, is mixed with 2 c.c. of nitric acid (sp. gr. 1·2), and after being diluted to 120 c.c., electrolysed with 3—4 cells. The precipitated copper is perfectly free from cadmium. The other portion is mixed with 12 grams of potassium cyanide and electrolysed with three cells. Cadmium, free from copper, is deposited.

Copper from Nickel.—The solution, which should contain no more than 0·5 gram of metal, is mixed with 1 c.c. of nitric acid, diluted to 120 c.c., and electrolysed with three cells. The copper deposit is treated with the usual precautions, and the liquid contains the nickel, which may be recovered by electrolysing with four or six cells, after the addition of 20 c.c. of a saturated solution of ammonium sulphate and 25 c.c. of ammonia; but the author generally works as follows:—An aliquot part of the original solution is acidified with three drops of sulphuric acid, and the copper is precipitated by hydrogen sulphide. The filtrate, after the addition of 20 c.c. solution of hydrogen peroxide, is evaporated to about 60 c.c., mixed with ammonium sulphate and ammonia, and then electrolysed. L. DE K.

Supersaturation of Solutions of Oxygen in Water. By C. A. SEYLER (*Chem. News*, **67**, 87).—Experiments made with the water of the Swansea supply, which is soft and organically pure, show that the temperature may be raised from 1° to 9·5°, or from 13° to 26·5°, without noticeable effect on the dissolved oxygen, the gaseous solution remaining supersaturated until shaken vigorously, when it parts with its excess of oxygen. D. A. L.

Source of Error in the Ultimate Analysis of Organic Substances. By G. S. JOHNSON (*Chem. News*, **67**, 99).—Neumann's observations concerning the hydrogen occluded by copper turnings on the results of hydrogen estimations confirm those published by the author (this Journal, 1876, i, 178, and Trans., 1879, 232). The author obviates this error by selecting copper as free from sulphur as possible; by alternately oxidising and reducing the copper many times before using, and by adopting the following arrangement and procedure in the combustion: the reduced copper for the reduction of the nitrogen oxides is placed in the front part of the tube and is followed in backward order by granulated copper oxide, a boat with the substance, a second boat with reduced copper, and a third boat with fused potassium chlorate. The whole is heated to redness, except the boats containing the substance and the chlorate, and before adjusting the weighed apparatus in front, a slow stream of dried air is passed, until the copper behind the substances is oxidised. The combustion is then proceeded with. D. A. L.

Detection of Nitrobenzene. By J. MARPURGO (*Zeit. anal. Chem.*, **32**, 235; from *Pharm. Post*, **23**, 258).—In a porcelain basin are placed two drops of liquid phenol, three drops of water, and a fragment of potash, as large as a pea. The mixture is boiled, and the aqueous solution to be tested is added. On prolonged boiling, nitro-

benzene produces at the edges of the liquid a crimson ring, which, on addition of a solution of bleaching powder, turns emerald-green. To examine a soap, it is dissolved in water, treated with excess of milk of lime, extracted with ether, and the residue of the ethereal solution tested as above. Oil of bitter almonds, warmed with manganese peroxide and sulphuric acid, loses its characteristic odour, whilst that of nitrobenzene remains unaffected. M. J. S.

Analysis of Creosotes. By A. Béhal and E. Choay (*Compt. rend.*, **116**, 197—200).—See this vol., i, 320.

Gas-volumetric Estimation of Organic Acids. By H. Kux (*Zeit. anal. Chem.*, **32**, 129—163).—The author has investigated the conditions under which the commoner organic acids can be estimated by Baumann's gas-volumetric iodine process (Abstr., 1892, 539). The general conditions essential to success are purity of the reagents, an approximate adjustment of the proportions, as, for example, for an evolution of 50 c.c. of oxygen there should be used about 2 grams of potassium iodide, 0·2 gram of iodate, not more than double the theoretical quantity of hydrogen peroxide, and between twice and ten times the theoretical amount of potash (solution of 1 part potassium hydroxide in 1 part of water), and lastly, extreme rapidity in mixing the iodine solution with the alkaline hydrogen peroxide. The apparatus used was Wagner's modification of Knop's azotometer, the reaction vessel consisting of a flask with a short, wide tube, fused to its bottom. In the outer chamber are placed the iodide, iodate, and acid to be estimated, diluting the whole to between 40 and 50 c.c. In the tube is placed a cooled mixture of 2—3 c.c. of hydrogen peroxide (2—3 per cent.) and 4 c.c. of the potash. After equalisation of temperature, the liquid in the flask is brought into rotation, and the contents of the tube suddenly mixed with it by inclining the flask, but without stopping the rotation. The whole reaction is over in 15 seconds, and after 10 minutes' cooling the volume of oxygen is read off.

The action of the organic acids on the iodide and iodate is in most cases slower than that of mineral acids. It can be accelerated by heat, in which case the mixture should be enclosed in a well-stoppered bottle, and plunged into water of 70—80°. Formic acid requires a digestion of half an hour in the cold, heating or longer digestion being inadmissible. Acetic acid requires two hours in the cold, or 10—15 minutes at 70°. Tartaric and citric acids require three hours in the cold, or 10—15 minutes at 70°. Propionic acid, three hours cold, or one hour hot. Malic acid, four hours cold, or 10—15 minutes hot. Butyric and succinic acids, 12 hours cold, or half an hour hot. Oxalic acid, lactic acid, and potassium hydrogen oxalate act instantly without heat, and potassium hydrogen tartrate requires 10—15 minutes at 70°. Iodic acid can be estimated by the same method, a small excess of a mineral acid being employed to liberate it. M. J. S.

The Reichert Process. By H. D. Richmond (*Analyst*, **18**, 64—65).—Wilson has shown that the rate of distillation of dilute

acetic acid is influenced by the salts in the solution distilled, and argues from the analogy between acetic acid and the acids from butter, that, therefore, the Reichert distillation process must be inaccurate.

The author replies that, however scientifically correct Wilson's views may be, in practice, the error is quite negligible.

L. DE K.

Estimation of Insoluble Fatty Acids. By C. E. CASSAL (*Analyst*, **18**, 44—45).—The use of a filter in the process of washing insoluble fatty acids in butter or other fats being cumbrous and liable to introduce errors, the author prefers to wash these acids in a globular separator made of thin glass, which will stand boiling water.

L. DE K.

Preservation of Milk for Analysis. By J. A. ALÉN (*Bied. Centr.*, 1892, 549—550).—It is frequently more convenient to analyse several samples of milk as one, and to enable this to be done without the milk turning sour, after being kept for days, potassium dichromate is to be added. The milk will then remain good, and further samples may be added to the first day after day. Five grams is sufficient for 250—500 c.c. of milk, the mixture being preserved in closed vessels at a temperature not exceeding +50°. This method, which the author intends patenting, allows of an accurate average composition being obtained.

E. W. P.

Leffmann and Beam's Method of Estimation of Milk Fat. By H. D. RICHMOND (*Analyst*, **17**, 144—152).—The author has made a thorough mathematical and chemical investigation of this process (Abstr., 1892, 1532), and thinks it may be classed among the trustworthy methods.

A source of error, although inappreciable, may be introduced by the presence of lactic acid.

L. DE K.

Estimation of Fat in Milk. By L. LIEBERMANN and S. SZÉKELY (*Zeit. anal. Chem.*, **32**, 168—173).—It was pointed out in 1885 by one of the authors (*Pharm. Centralhalle*, 1885, 253) that ether extracts from milk other substances besides fat. The residue from the evaporation of the ethereal solution is no longer wholly soluble in ether, and the results of extraction with light petroleum are always lower than those with ether. The following method, which is very rapid, gives results differing only in the second decimal from those obtained by complete exhaustion with petroleum. 50 c.c. of milk, at the temperature of the laboratory, is placed in a cylinder 25 cm. high and of 4·5 cm. diameter. 5 c.c. of potash (sp. gr. 1·27) is added, and, after inserting a cork, the whole is well shaken. There is next added 50 c.c. of light petroleum (sp. gr. 0·663 and boiling at about 60°), and the mixture is shaken until an emulsion forms. 50 c.c. of 96 per cent. alcohol is then added and again shaken. In four or five minutes, the petroleum will have completely separated. The shaking is repeated at least three times, for a quarter of a minute each time, and with sufficient intervals for complete separation. 20 c.c. of the petroleum layer is now withdrawn by a pipette and evaporated in a tared

vessel, drying the residue at 110—120°. The weight, multiplied by 5, and corrected for the specific gravity of the milk, gives the percentage of fat. M. J. S.

Iodine Absorption. By F. Gantter (*Zeit. anal. Chem.*, **32**, 178—181 and 181—184).—In order to investigate the influence which the addition of mercuric chloride in Hübl's process has on the absorption of iodine by unsaturated fatty substances, the author employed a solution of iodine in carbon tetrachloride, and dissolved the fat directly in the iodine solution after the addition of varying quantities of mercuric chloride. Under these conditions, the percentage of iodine absorbed by linseed oil rises with the increase in the amount of mercuric chloride, being, when the excess of iodine was small, 83·5 per 100 parts of oil when the mercuric chloride was 50 per cent., and 148 per 100 when the amount of mercuric chloride was increased tenfold. With a large excess of iodine, a similar variation took place, as much as 188 per cent. being absorbed when 6 parts of iodine and 10 of mercuric chloride were employed for 1 part of oil, and at the same time the percentage absorption varied with the amount of iodine used, when the mercuric chloride was kept constant. Lard exhibited similar phenomena, and even saturated compounds, such as lauric and stearic acids, which in the absence of mercuric chloride absorb no iodine, show, when mercuric chloride is added, a small absorption, rising with increased amounts of mercuric chloride. In conducting Hübl's process, it is therefore necessary that the conditions be kept absolutely constant, and even then the results have only a relative value.

In order to avoid the complications introduced, and the excessively high results obtained, by the addition of mercuric chloride (see above), it is necessary to employ a menstruum in which both iodine and fats are freely soluble. Carbon tetrachloride fulfils these requirements. With small excesses of iodine, the absorption is extremely sluggish, but by employing 4 or 5 parts of iodine for 1 part of fat, the absorption is complete in about 50 hours, and concordant results are obtained. The iodine solution recommended contains 10 grams per litre. In making this solution, the iodine should not be dissolved in the graduated flask itself, since the opacity of the liquid does not allow of ascertaining when solution is complete. The iodine solution is titrated by one of sodium thiosulphate containing 19·528 grams per litre, the two solutions being shaken together in a well-stoppered bottle, with starch indicator towards the end.

Of drying oils 0·1 gram, of other fats 0·2 gram, is weighed into a stoppered bottle; 50 c.c. of the iodine solution is added, and the mixture shaken until the oil is completely dissolved. Sufficient water is then added to form a layer several millimetres thick on the surface, the stopper is inserted, and the whole allowed to react at the ordinary temperature for 50 hours. The residual iodine is then titrated as before. At lower temperatures, higher numbers are obtained, and conversely. A single estimation of the iodine absorption of linseed oil reported shows only 76·2 per cent. M. J. S.

Contributions to the Analysis of Fats. By J. Lewkowitsch (*J. Soc. Chem. Ind.*, **11**, 134—145; compare Abstr., 1891, 509, and 1892, 544).—*Sperm Oil.*—The higher alcohols contained in sperm oil were prepared in the usual way by saponifying a pure specimen of the latter with alcoholic potash, when 41 per cent. of unsaponifiable substances were obtained. The alcohols were then converted into the corresponding acetates by boiling with acetic anhydride, and the mixture of acetates was subjected to fractional distillation in a vacuum. Four fractions of about equal amount were obtained between 295° and 315°, having the saponification values 187·7, 185·0, 183·0, and 168·0 respectively. These figures do not bear out Allen's assertion that sperm oil contains alcohols of the formulæ $C_{13}H_{28}O$ and $C_{15}H_{32}O$, for the acetates of dodecatyl and pentadecyl alcohols have the saponification values 246 and 207·7 respectively. The alcohols prepared from the acetates all solidified on cooling. The saponification values show that these alcohols, or any way large percentages thereof, belong to alcohols of the unsaturated series.

Quantitative Estimation of Cholesterol.—It was found that the formation of cholesteryl acetate and cholesterol diiodide is quantitative, their production affording an easy means for the quantitative estimation of cholesterol and isocholesterol. D. B.

Estimation of Urea. By W. Colquhoun (*Chem. News*, **67**, 123).—The author's apparatus is mounted on a stand, and consists of an inverted, stoppered burette, graduated from the stopcock to show tenths of a cubic centimetre; the other end is attached by india-rubber tubing to a tube provided with two side tubes, and having below the lower side tube an enlargement of 15 c.c. capacity, below which is a stopcock and another bulb of 6 c.c. capacity with another stopcock beneath it; the side tubes are connected, by india-rubber tubing furnished with clips, to two reservoirs, one containing water, the other hypobromite or hypochlorite. To use the apparatus, the lowest stopcock is closed and the intermediate one withdrawn, the urine is then introduced, by means of a special graduated pipette, into the lower bulb, the intermediate stopcock is replaced and turned off; the required quantity of hypobromite is now admitted into the larger bulb, and finally the rest of this bulb and the burette are filled with water. The uppermost stopcock being then closed, the analysis is completed by steadily running the hypobromite into the urine and subsequently measuring the nitrogen. The whole apparatus and materials should of course be at the temperature of the laboratory. To obviate repeated corrections for temperature, pressure, and tension of aqueous vapour, a table is furnished showing the quantity of urine which, under any indicated temperature and pressure, will evolve as many cubic centimetres of nitrogen as the urine contains grams of urea per litre. Good results have been obtained by the author.

D. A. L.

Estimation of Quinine in Cinchona Barks. By J. H. Schmidt (*Chem. Centr.*, 1892, ii, 946—947; from *Pharm. Centralhalle*, **33**, 594—595).—20 grams of air dried, finely powdered bark is treated

for 24 hours with 10 c.c. of 10 per cent. ammonia, 20 c.c. of 90 per cent. alcohol, and 170 c.c. of ether, with repeated agitation. 100 c.c. of the liquid is then placed in a beaker, 27 c.c. of water and 3—4 c.c. of normal hydrochloric acid added, and the whole set aside for 24 hours to evaporate spontaneously. The residual liquid is then heated on the water bath to remove alcohol and ammonia, and neutralised with hydrochloric acid. If the liquid is too acid, the excess must be neutralised with cinchonine, not with ammonia or potash. With very rich *Ledgeriana* barks, 1—2 c.c. of acid may be necessary for the complete dissolution of the alkaloïds. The supernatant liquid, which amounts to about 15 c.c. is exposed to the air, in order to precipitate a red colouring matter, filtered when clear, 2—3 grams of Rochelle salt added, heated for 15 minutes on the water bath, and then set aside for 24 hours. The precipitated tartrates are then collected, and washed by suction, with the smallest possible quantity of water. If all the quinine and cinchonidine are precipitated, the mother liquor will not give any turbidity when warmed with Rochelle salt. An allowance must be made of 0·0008 gram of quinine for each c.c. of mother liquor and 0·0004 gram for each c.c. of wash water. The tartrates are then dissolved in water containing hydrochloric acid, and repeatedly shaken with ether, until the latter is no longer coloured. The alkaloïds are then precipitated with soda, and extracted by repeated agitation with ether; the ethereal extract being evaporated, dried at 100—110°, and weighed. With *Cinchona succiruba* and *C. officinalis*, the residue invariably contains cinchonidine, but this is not the case with rich *Ledgeriana* bark. The residue is, therefore, treated with a saturated ethereal solution of cinchonidine, which dissolves the quinine only; the ethereal extract is carefully decanted, the residue washed with a few c.c. of pure ether and again weighed, the loss of weight giving the amount of quinine. From the ethereal solution, the quinine can also be readily obtained as the pure white tartrate, and its amount estimated either by the polariscope or by de Vrij's method. A. J. G.

Estimation of Tannin in Wine. By T. Chiaromonte (*Staz. Sper. Agrar.*, **20**, 337—350).—Numerous experiments are described, undertaken in order to clear up some points in connection with the estimation of tannin by the permanganate method. Tannin solutions of known strength, and afterwards wines, were employed. The points specially studied were the effect of the amount of ammonia employed; whether the action of ammonia on the zinc tannate is oxidising or solvent; the effect of the amount of zinc acetate employed on the precipitation of zinc tannate, and finally the influence on the results of the mode of applying heat. It was found that ammonia plays an important part in the precipitation, but it both slightly dissolves and oxidises the zinc tannate, and on this account too much must not be used. An excess of zinc acetate was also found to cause a slight loss. Heating is necessary for complete precipitation, but it must be by means of a water bath, and should only be continued for a few minutes.

The following modification is recommended: 50 c.c. of wine (or 25 c.c. if much tannin is present) is evaporated on a water-bath to about one-third, made distinctly alkaline with ammonia, and treated with zinc acetate solution (10—15 c.c.) and 10 per cent. ammonia (2 c.c.). The whole is heated for a few minutes on a water-bath, allowed to cool, filtered quickly through a folded filter, and the precipitate washed with cold water. The zinc tannate is quickly dissolved in dilute sulphuric acid (15 c.c.); indigo-carmine solution (20 c.c.) is added, and the whole made up with water to about 400 c.c.; to this the permanganate solution is gradually added, until the colour changes from greenish to gold colour. With pure indigo, the change is instantaneous, and with practice great exactness may be obtained.

The solutions employed were of the following strengths: permanganate, 0·2 per cent.; zinc acetate, 1 per cent.; sulphuric acid, 20 per cent. (compare Martelli, *Staz. Sper. Agrar.*, **18**, 324; Vigna Abstr., 1891, 1399). N. H. M.

The Chemico-legal Examination of Suspected Blood Stains. By H. Struve (*Zeit. anal. Chem.*, **32**, 174—178).—The author confirms the observation of Janeček (Abstr., 1892, 1369), that hæmin crystals can be obtained from the excrement of flies which have been fed with blood, but on treating the flies themselves with alcohol (70 per cent.) and with ammoniacal alcohol, he was unable to observe any trace of the characteristic absorption spectrum of blood.

M. J. S.

Detection of Horse Flesh in Food. By W. Niebel (*Bied. Centr.*, 1893, 126).—The excess of glycogen present in horse flesh over that which is contained in the flesh of other animals is employed as the means whereby an admixture of horse flesh may be detected. Moreover, as glycogen gradually changes into grape sugar, it is necessary to estimate also the amount of sugar present in the food. E. W. P.

General and Physical Chemistry.

Spectra of Aluminium, Indium, and Thallium. By H. KAYSER and C. RUNGE (*Ann. Phys. Chem.* [2], **43**, 126—149).—Continuing their researches on the line spectra of the elements (Abstr., 1891, 137 and 965), the authors have now investigated metals of the third group of the periodic system. Boron gives only two lines, of wave-lengths 2497·80 and 2496·84, and the rare earths and gallium were omitted from examination on account of the difficulty of obtaining the necessary material. The lines in the spectra of the remaining three elements, aluminium, indium, and thallium, may be arranged in two series of pairs of lines, the reciprocals of whose wave-lengths are given by the general formula $A - Bn^{-2} - Cn^{-4}$. In this formula, the values of the constants are:

	First Series.			Second Series.		
	A.	B.	C.	A.	B.	C.
Al.....	48308·2	156662	2505331	48244·5	127527	687819
In	44515·4	139308	1311032	44535·0	126766	643584
Tl	41542·7	132293	1265223	41506·4	122617	790683

These numbers give the first of the lines in each of the pairs. As there is a constant difference between the wave-lengths of lines in pairs of the same series, it is only necessary to alter the constant A to obtain the second lines of the pairs. The new values of the constant will then be:

	Al.	In.	Tl.
First Series	48420·2	46728·6	49307·6
Second Series	48356·5	46748·2	49301·3

H. C.

Ultra-red Spectra of the Alkalis. By H. KAYSER and C. RUNGE (*Ann. Phys. Chem.* [2], **48**, 150—157).—A criticism of Snow's paper (this vol., ii, 58) in which the authors claim that impurity of the material used is the probable cause of the discrepancy between the above observers' results and their own calculations in certain cases.

H. C.

Absorption Spectra of Chromium Compounds. By W. LAPRAIK (*J. pr. Chem.* [2], **47**, 305—342).—The absorption spectra of the salts $M'_6Cr_26C_2O_4$ are the same whether the salts be in solution

or as solids, but in the latter case the absorption bands are shifted towards the less refrangible end.

Chromium oxalate gives an absorption spectrum which differs from those shown by the double salts. But a solution of chromium oxalate with a small excess of oxalic acid gives the same absorption spectrum as that given by Croft's salt, $K_2Cr_24C_2O_4$, and with a large excess a spectrum identical with that of the salts $M_6Cr_26C_2O_4$, showing that a hydrogen salt corresponding with these exists in the solution.

The absorption spectra of the corresponding oxalates of iron, manganese, and cobalt are not analogous.

The corresponding *potassium chromium malonate*, $K_6Cr_36C_3H_2O_4 + 6H_2O$, was prepared, and its absorption spectrum is described. An analogous succinate could not be obtained.

The absorption spectra of solutions of chromium hydroxide in various organic acids are collated, and it is shown that in the case of the fatty acids the spectra are similar, but the bands are shifted towards the less refrangible end of the spectrum as the molecular weight increases.

The band 710—692 is characteristic of all the compounds examined, save potassium chromium cyanide, but is not absolutely identical in every case. The general absorption in the green, 650—550, is also universal. A. G. B.

An Electrical Furnace. By H. Moissan and J. Violle (*Compt. rend.*, **126**, 549—551).—The furnace consists of a carbon receptacle in which the arc from two horizontal electrodes acts on the substance in the furnace. The receptacle is a portion of a carbon tube, the height of the segment being equal to its diameter, and it stands upon a carbon plate and is covered with a disc of the same substance. The electrodes also consist of carbon, and all the carbon parts of the apparatus are prepared from powdered gas carbon and tar, without any boric acid. The carbon cylinder and electrodes are enclosed in a block of lime, from which they are separated by a layer of air 5 mm. in thickness; the cylinder being supported on props of magnesia. The dimensions of the furnace and of the electrodes depend on the power of the current and the temperature that is desired: but there is no difficulty in obtaining a temperature of 3000°. C. H. B.

Behaviour of Solid Colloïdal Silver towards the Electric Current. By C. Barus and E. A. Schneider (*Ann. Phys. Chem.* [2], **48**, 327—337).—The previous determinations of the conductivity of colloïdal silver made by the authors (Abstr., 1891, 1412) not agreeing with the results obtained by Oberbeck, the experiments have been repeated, and the former conclusions have been thus in every way confirmed. H. C.

New Method of determining the Melting Point of Inorganic Substances. By A. Potilitzin (*J. Russ. Chem. Soc.*, **24**, 1—23).—After discussing at considerable length the means which have been adopted for determining the fusing point of substances melting (*a*) below 300°, and (*b*) above 300°, the author gives the following

method for finding the temperature of fusion for substances which melt not higher than 450°, the highest temperature which a nitrogen-filled mercury thermometer can indicate. A hard glass tube, of about 5 mm. bore and 500—600 mm. long, is drawn out to capillary fineness at one end, and bent at right angles about 150 mm. from the other end. The capillary is dipped into the molten substance, the melting point of which is to be determined; so that, on cooling, the tube is closed by a solid plug of the substance 3—4 mm. long. The other end is connected with a manometer by means of which a pressure exceeding that of the atmosphere is maintained within the tube. The tube, along with the principal thermometer, and one for stem correction, is inserted into a wide test-tube, which is then immersed in a bath of fusible metal; when the melting point is reached, the plug softens and is expelled by the excess of pressure inside the tube, so that the sudden equalising of pressure in the manometer indicates the moment at which the substance melts, the thermometers being then read off. Potassium nitrate was found by this method to melt at 336·57° (mean of eight experiments ranging from 336·40° to 336·71°): by immersion of the thermometer direct into a large mass of the salt, the melting point was found to be 336·0°. J. W.

Nature of Solutions. By A. Reychler (*Bull. Soc. Chim.* [3], **7**, 812—819).—After pointing out difficulties in the way of accepting the Arrhenius' theory of electrolytic dissociation in solutions, the author proposes to substitute for it the view that salt molecules undergo hydrolytic dissociation in dilute solution. An explanation of the mechanism of electrolysis is given based upon this view. H. C.

Influence of Gravity on the Concentration of Solutions. By V. Turin (*J. Russ. Chem. Soc.*, **24**, 90—91).—The author has developed the following formula to express the influence of gravity on the concentration of a solution

$$hg = \frac{p_0}{\sigma_0} \cdot \log \frac{\sigma}{\sigma_0} \cdot \frac{1}{\left(\frac{\partial \sigma}{\partial \rho}\right)},$$

in which h is the depth, p_0 the osmotic pressure at the depth $h = 0$, σ_0 the concentration at h_0, σ the concentration at h, ρ the density of the solution corresponding to the concentration σ. In J. J. Thomson's formula $\partial\sigma/\partial\rho = 1$, that is, the tacit assumption is made that the volume of solution containing 1 gram of solvent is equal to the volume of 1 gram of the pure solvent. The author suggests experimental verification by rotating a long tube, filled with solution, radially round an axis revolving at a high speed. J. W.

Electric Conductivity and Freezing Point of Aqueous Solutions of Fluorine Compounds. By R. Speransky (*J. Russ. Chem. Soc.*, **24**, 304—309).—All ferric salts which are electrolytically dissociated give yellow aqueous solutions; those which are hydrolytically dissociated give reddish-brown solutions. As aqueous solu-

tions of ferric fluoride are colourless, it seemed probable that neither electrolytic nor hydrolytic dissociation played any part in them, and the author has instituted experiments to ascertain if this view is correct. The electrical conductivity of the solutions is very small, so that there can be no appreciable electrolytic dissociation. The practical absence of hydrolytic dissociation is demonstrated by the fact that the solutions scarcely effect any inversion of cane sugar. Determinations of the freezing point give a molecular weight for dilute solutions nearly corresponding with the formula FeF_3. In more concentrated solutions, there are indications of the existence of complex molecules, probably Fe_2F_6.

Similar experiments were made with chromic fluoride and aluminium fluoride. In their case also, the molecules existing in aqueous solution are predominantly CrF_3 and AlF_3, although there is slight electrolytic dissociation and also aggregation to Cr_2F_6 and Al_2F_6 molecules. The violet modification of chromic fluoride conducts electricity much better than the green modification. J. W.

Dissociation of Sodium Chloride in presence of Heated Surfaces of Porous Clay. By DE SANDERVAL (*Compt. rend.*, **116**, 641).—When a tube of porous earthenware is heated in an atmosphere of sodium chloride vapour mixed with dry air, the interior of the tube becomes filled with chlorine, whilst only traces of this gas exist in the atmosphere outside the tube. Chemical action takes place between the sodium chloride and the silica of the tube, and there is also dissociation under the influence of heat. The evolution of chlorine ceases as soon as the pores of the tube are closed by the formation of a glaze of silicates on its external surface. The theory of these changes was explained by the author in 1886.

C. H. B.

Rate of Diffusion of Dextro- and Lævo-rotatory Tartaric acid. By L. MARCHLEWSKI (*Ber.*, **26**, 983—984).—A tube about 90 cm. long, packed with six rolls of filter paper, was placed vertically, with the lower end in a 6 per cent. solution of racemic acid, and removed as soon as the top roll became wet, the experiment being then repeated several times. Neither the residual solution nor that absorbed by the filter paper showed optical activity; hence the molecules of dextro- and lævo-rotatory tartaric acid (into which the molecules of racemic acid are completely dissociated in dilute solution) must have diffused with equal rapidity. C. F. B.

Determination of the Atomic Weight by the Method of Limit. By G. HINRICHS (*Compt. rend.*, **116**, 753—756).—In atomic weight determinations, the errors increase with the amount of substance employed. To obtain the true atomic weight, a series of determinations should be made with gradually increasing amounts of material, and the atomic weight calculated not from the mean of all determinations, but from the limiting value corresponding with zero weight of substance. The author recalculates Dumas' determinations of the composition of water by this method, and obtains $H = 1$ for $O = 16$. H. C.

General Method for the Calculation of the Atomic Weight from the Data of a Chemical Analysis. By G. HINRICHS (*Compt. rend.*, **116**, 695—698).—The ordinary method of determining atomic weights is to fix one of them, say A, arbitrarily, and from this to determine the others, $B = k_1A$; $D = k_2B = k_1k_2A$; and finally, $x = k_1k_2 \ldots k_nA$. In this method all the quantities k contain unknown errors, and the constant accumulation of these errors will, in the end, prevent all chance of exactness. Since, when O = 16, most of the atomic weights approximate to whole or half numbers, the author proposes the following method for calculating atomic weights, as being free from the above objection. Suppose A, B, ..., X to be the true atomic weights, and A_0, B_0, ..., X_0 to be the whole numbers nearest to each, then

$$A = A_0 + a,\ B = B_0 + b,\ \ldots,\ X = X_0 + x,$$

where a, b, ..., x, are small numbers compared with A_0, B_0, ..., X_0. Let α, β, ..., ξ be the coefficients corresponding to the unit of weight, then

$$A = A_0(1 + \alpha),\ B = B_0(1 + \beta),\ \ldots,\ X = X_0(1 + \xi).$$

From this the ratio $X/A = X_0/A_0(1 + \xi - \alpha)$. H. C.

Inorganic Chemistry.

Action of Ammonia on Hypochlorites. By J. THIELE (*Annalen*, **273**, 160—163).—When a sufficiently dilute solution of sodium hypochlorite is treated with ammonia in the cold, evolution of gas does not take place, and the mixture, although still containing a considerable quantity of hypochlorite, has powerful reducing properties. A solution prepared in this way slowly reduces ammoniacal silver solutions in the cold, more quickly on warming, and precipitates cuprous oxide from solutions of copper salts; it rapidly reduces potassium permanganate to manganous oxide on heating, and at the same time it decolorises indigo solution. On evaporating such a solution to dryness, the residue is without reducing power; when, however, a solution prepared by adding chlorine water to ammonia is distilled under reduced pressure, the distillate has powerful reducing properties, but not if the solution be treated with soda before distilling.

Attempts to ascertain whether the reducing properties of such solutions were due to the presence of hydroxylamine or hydrazine were unsuccessful. F. S. K.

Influence of Temperature on the Formation of Ozone. By A. BEILL (*Monatsh.*, **14**, 71—80).—The author finds that the percentage volume of oxygen converted into ozone is only increased very

slightly by considerably lowering the temperature. For example, oxygen, dried by calcium chloride, was found to contain 5·2 per cent. of ozone when passed through the ozoniser at a temperature of 20°; whilst at temperatures of 0°, −20°, −46°, and −73°, the percentages formed were 6·8, 7·8, 9·2, and 10·4 respectively. The author gives a description of the apparatus and of the method employed, and has plotted out his results in the form of curves. G. T. M.

Selenium Compounds. By W. Muthmann and J. Schäfer (*Ber.*, **26**, 1008—1016).—*Seleniobromides.*—By dissolving selenious anhydride in hydrobromic acid, adding potassium or ammonium bromide, and concentrating the solution, regular octahedral crystals of the salts K_2SeBr_6 or $(NH_4)_2SeBr_4$ are respectively obtained, isomorphous with the analogous tellurium and platinum compounds. They are orange-red in colour, but are decomposed by water into selenious acid, hydrobromic acid, and alkali bromide, yielding a colourless solution. Neither a sodium nor a silver compound could be prepared.

Chloro- (and bromo-) pyroselenites.—When an attempt is made to procure analogous chlorine compounds, colourless, monoclinic crystals of a compound $M'Cl,2SeO_2,2H_2O$ are obtained; these were prepared in the cases M′ = K, NH_4, and Rb. When the mother liquor from the above-mentioned potassium seleniobromide is allowed to evaporate slowly, crystals of the salt $KBr,2SeO_2,2H_2O$ are deposited; the corresponding ammonium compound was also prepared. If a solution of the potassium chlorine salt is treated with silver oxide, the solution filtered from silver chloride, and evaporated, crystals of Nilson's potassium tetraselenite, $KHSeO_3,H_2SeO_3$, are deposited. It is suggested that the substance, since it loses only two-thirds of its water at 100°, is really potassium hydrogen pyroselenite,

$$KO{\cdot}SeO{\cdot}O{\cdot}SeO{\cdot}OH + H_2O;$$

the original compound, from which this was derived by substituting OH for Cl, would then be potassium chloropyroselenite,

$$KO{\cdot}SeO{\cdot}O{\cdot}SeO{\cdot}Cl.$$

Estimation of Selenium.—This may be effected with tolerable accuracy by adding a hydrochloric acid solution of potassium iodide) with which selenious acid yields iodine, selenium, and water) and titrating the iodine with thiosulphate solution; the presence of selenium rather obscures the end-reaction with starch. C. F. B.

Hydroxylamine. By W. Wislicenus (*Ber.*, **26**, 771—774).—It has been shown by V. Meyer that hydroxylamine sulphate and sodium nitrite in concentrated aqueous solution undergo mutual decomposition at the ordinary temperature with rapid evolution of nitrous oxide; in dilute solution, the action also takes place on heating, but at lower temperatures the decomposition only proceeds slowly, and on treating the solution with silver nitrate a yellow precipitate of silver hyponitrite, $Ag_2N_2O_2$, is formed, and may be purified by dissolving it in cold dilute nitric acid and reprecipitating with ammonia.

The production of hyponitrous acid may be shown as a lecture

experiment by dissolving hydroxylamine sulphate (2—3 grams) and the equivalent quantity of sodium nitrite separately in water—the total volume should not exceed 200 c.c.; the solutions are mixed and a portion tested with silver nitrate, a white precipitate of silver sulphate and silver nitrite being produced; the remainder of the solution is quickly heated to 50° on the water-bath for a few moments, the evolved gas being tested with a glowing splint of wood; on adding silver nitrate to the warm solution, a yellow precipitate of silver hyponitrite will be formed. The exact time during which the heating should be continued may be readily ascertained by a preliminary experiment. J. B. T.

Properties of Diamonds. By H. Moissan (*Compt. rend.*, **116**, 460—463).—The author has determined by means of a Le Chatelier thermo-electric couple the temperature at which diamonds begin to burn in oxygen. When the temperature is raised slowly, the combustion of the diamond takes place slowly and without recognisable evolution of light, its occurrence being indicated only by the action of the issuing gas on baryta solution. At 40° to 50° above the point at which this slow combustion takes place, the combustion becomes rapid, and a distinct flame is visible. The following results were obtained with eight different specimens:—Yellowish-brown carbonado burned with a flame at 690°; black carbonado with a flame at 710—720°; transparent Brazilian diamond, without a flame, at 760—770°; transparent crystallised Brazilian diamond, without a flame, at 760—770°; cut diamond from the Cape, without a flame, at 780—790; Brazilian bort, without a flame, at 790°, and with a flame at 840°; Cape bort, without a flame, at 790°, and with a flame at 840°; very hard bort, without a flame, at 800°, and with a flame at 875°. As a rule, the harder the diamond, the higher its ignition point.

When heated in hydrogen at 1200°, Cape diamonds undergo no loss in weight, although they may become somewhat lighter in colour, and lose their transparency; dry chlorine and dry hydrogen fluoride have no action at 1100—1200°. Sulphur vapour attacks diamonds only at 1000°; but with carbonado, carbon bisulphide is readily produced at 900°. Sodium vapour has no action at 600°. Iron at its melting point attacks the diamond readily, and graphite separates on cooling; melted platinum also combines with it readily. Fused potassium hydrogen sulphate and the alkali sulphates have no action, and calcium sulphate is not reduced even at 1000°. Fused potassium chlorate and potassium nitrate have no action on the diamond; but Damour has shown that carbonado is attacked under these conditions.

When heated with alkali carbonates at a high temperature, the diamond is rapidly dissolved, with production of carbonic oxide. No hydrogen is, however, given off, and hence the author concludes that diamonds contain neither hydrogen nor hydrocarbons.

C. H. B.

The Ash of Diamonds. By H. Moissan (*Compt. rend.*, **116**, 458—460).—The diamonds were treated with hydrofluoric acid, and

then with aqua regia, and were afterwards washed, dried, and burnt in oxygen. In all cases, except one, the ash was composed chiefly of ferric oxide. Bort from the Cape contained also silica, calcium, and magnesium; whilst Brazilian carbonado contained silica and calcium, but only very minute traces of magnesium.

One specimen of green, transparent bort from Brazil left a very minute quantity of ash, which contained silica, but no iron.

C. H. B.

Graphite and Graphitite. By W. Luzi (*Ber.*, **26**, 890—895).—In previous papers (Abstr., 1892, 406, 945), the author has shown that the varieties of carbon usually classed as graphite may be divided into two classes, according as they swell up on moistening with strong nitric acid and igniting or not. He proposes to retain the name graphite for the first class, and to term the varieties which do not show the reaction graphitite. In the present paper, it is shown that the two classes also behave in a different manner towards other reagents. Graphite from three different sources, when treated with concentrated nitric acid and potassium chlorate, yields the so-called graphitic oxide in thin, transparent, laminated crystals which, on heating, swell up very considerably, forming a loosely-aggregated mass of fine threads, termed by the author pyrographitic oxide. Graphitite from varying sources, on the other hand, gives a graphitite oxide which consists of a powder, showing no crystalline form, and on heating does not swell up, but yields pyrographitic oxide as a fine powder.

H. G. C.

Intumescent Graphite. By H. Moissan (*Compt. rend.*, **116**, 608—611).—Luzi observed that when certain specimens of natural graphite are moistened with nitric acid and heated, they swell up and form dendritic or vermiform masses, whilst other specimens do not show this behaviour; the former he proposed to call graphites, and the latter (which include carbon from cast iron and from the electric arc) graphitites. Luzi obtained intumescent graphite from Ticonderoga, Quebec, Ceylon, Spain, Norway, and many other localities, and the author has found it in the blue earth from the Cape Diamond Fields (this vol., ii, 285).

When molten cast iron is rapidly cooled by means of water, the external layer of the ingot contains ordinary graphite, but the layers below contain the intumescent graphite as well.

In order to obtain the intumescent variety alone, platinum is melted in a carbon crucible in an electric furnace. It melts rapidly, and, after a few minutes, distils and condenses in fused drops on the colder part of the electrodes. After five minutes, the current is cut off, the metal is allowed to cool in the carbon crucible, and the platinum is dissolved by repeated treatment with aqua regia, the residue, which amounts to 1·45 per cent., being washed with water and dried.

The variety of graphite thus obtained forms hexagonal plates paler in colour than graphite from cast iron, and with parallel striæ and triangular markings in lower relief than those seen on diamonds; sp. gr. = 2·06 to 2·08. It burns in oxygen at 575°; at 400° it swells up in the same way as mercuric thiocyanate, and at a dull-red heat

intumesces abundantly. The light mass left after intumescence is graphite, and yields green graphitic oxide when treated with nitric acid and potassium chlorate, the product becoming pale yellow on a second treatment.

This variety of graphite is not attacked by potassium nitrate at its melting point, but at a higher temperature the graphite intumesces, and is afterwards destroyed somewhat rapidly, although rarely with incandescence. Fused chromic anhydride is practically without action, but at the moment of its decomposition a little carbonic anhydride is given off. On the other hand, iodic acid, when gently heated, attacks it readily, iodine and carbonic anhydride being given off. Fused sodium carbonate also attacks it rapidly, but sulphuric acid is without action, even when boiling.

Two analyses of the product obtained by means of platinum gave C, 99·02; ash, 1·10 = 100·12; and C, 98·94; ash, 1·02 = 99·96.

When the intumescence takes place, nitrogen oxides and a small quantity of carbonic anhydride are given off, but on a second treatment with the acid, only traces of the gas are evolved, and a third treatment is without any effect. It would seem, therefore, that the intumescence is due to a sudden evolution of gas, resulting most probably from the action of the nitric acid on small quantities of amorphous carbon enclosed between the lamellæ of the graphite.

C. H. B.

Preparation of Pure Rubidium Salts. By W. Muthmann (*Ber.*, **26**, 1019—1020).—Commercial "pure" rubidium salts contain small quantities of cæsium and potassium which it is difficult to detect by means of the spectroscope. To obtain a pure salt, commercial rubidium chloride (30 grams) is dissolved in very strong hydrochloric acid (250 c.c.) and antimony chloride (2·5 grams) dissolved in strong hydrochloric acid is added. The small precipitate (about 1·4 grams $RbSbCl_4$ and $CsSbCl_4$) is filtered off on an asbestos filter, the filtrate evaporated almost to dryness, the antimony still present removed with hydrogen sulphide, and the resulting mixture dissolved in strong hydrochloric acid. Rather more of a hydrochloric acid solution of stannic chloride is added than is necessary to form the stannichloride Rb_2SnCl_6; this substance is then precipitated, whilst potassium stannichloride, K_2SnCl_6, remains in solution. The precipitate is allowed to settle, washed several times by decantation, collected on an asbestos filter, dissolved in water, and the tin removed with hydrogen sulphide. The rubidium chloride so obtained is pure; 0·44 gram contained 29·30 instead of 29·34 per cent. of chlorine.

C. F. B.

Zinc and Cadmium Fluorides. By C. Poulenc (*Compt. rend.*, **116**, 581—584).—Crystallised and anhydrous zinc fluoride can be obtained by (1) the action of dry hydrogen fluoride on zinc at a red heat, (2) the action of dry hydrogen fluoride on fused zinc chloride at 800—900°, (3) the action of dry hydrogen fluoride on zinc oxide or on the hydrated fluoride at a red heat. It forms slender, colourless, transparent needles, which act strongly on polarised light, and seem to belong to the monoclinic or possibly the triclinic system; sp. gr. at 15° = 4·84. It is insoluble in alcohol of 95°, and is only slightly

soluble in cold water, but the solubility in water increases with the temperature. Boiling hydrochloric, nitric, or sulphuric acid dissolves it, hydrogen reduces it at a red heat, hydrogen sulphide converts it into zinc sulphide, and hydrogen chloride converts it into zinc chloride. When heated in air, or to redness in water vapour, it is completely converted into zinc oxide, and when fused with alkali carbonates, it yields zinc oxide and an alkali fluoride.

Anhydrous cadmium fluoride is obtained in the same way, but lower temperatures are required than in the case of zinc. It forms a colourless, translucent, "crackled" product of sp. gr. 6·64. It is somewhat soluble in water, but is insoluble in alcohol of 95°, and in all other properties is strictly analogous to the zinc compound.

C. H. B.

Cæsium and Potassium Lead Haloïds. By H. L. Wells (*Amer. J. Sci.*, **45**, 121—134).—As a continuation of the investigations on double haloïds (Abstr., 1892, 773; this vol., ii, 67), a study of the cæsium lead salts has been undertaken. The following salts have been established:—

Cs_4PbCl_6,	Cs_4PbBr,	—
$CsPbCl_3$,	$CsPbBr_3$,	$CsPbI_3$.
$CsPb_2Cl_5$	$CsPb_2Br_5$,	—

These results show the existence of three types of lead double haloïds.

The method of preparation, the properties of the salts, and the analytical methods employed are fully described. B. H. B.

Atomic Weight of Thallium. By C. Lepierre (*Compt. rend.*, **116**, 580—581).—The starting point in these determinations was pure crystallised thallic oxide, prepared by fusing the sulphate, nitrate, or chloride with pure potassium hydroxide. The estimations made were (1) weight of thallium from thallous sulphate by electrolysis (Tl = 203·52 to 203·69), (2) weight of thallium in thallic oxide, after conversion into sulphate and electrolysis (Tl = 203·53 to 203·73), (3) weight of thallic oxide from a known weight of thallous salts (Tl = 203·44 to 203·79), and (4) relation between the thallium and oxygen in thallic oxide as determined by reduction in hydrogen (Tl = 203·54 to 203·60). The mean of eleven determinations gave Tl = 203·62.

C. H. B.

As neither the standard nor any details as to the methods employed are given, it is impossible to form any opinion as to the value of the results. [Editors.]

Purification of Mercury. By W. Jäger (*Ann. Phys. Chem.* [2], **48**, 209—212).—After distillation in a vacuum in a specially constructed apparatus in which the use of grease for the taps or of india-rubber for the connections was avoided, the mercury was converted into mercurous nitrate and deposited electrolytically from a solution of this salt. A platinum electrode served as cathode, and as anode distilled mercury was used. A current of 1 to 3 ampères was used, this giving 0·004—0·012 ampère at the cathode and 0·001—0·003

ampère at the anode per sq. cm. The absence of heavy metals in the mercury finally obtained was ascertained by careful analysis.

H. C.

Samarium. By L. DE BOISBAUDRAN (*Compt. rend.*, **116**, 611—613 and 674—677).—The head products of a fractionation of Cleve's samarium by ammonia, which contain the greater part of Z_β and show the electrical rays Z_ϵ and the reversal band Z_ζ, were fractionated with oxalic acid. The head of this fractionation is white and does not show the reversal band Z_β, but the tail is yellow and shows Z_β, whilst the reversal spectra of samarium and Z_ζ and the electrical rays Z_ϵ have practically the same intensity in both the head and tail. No product was obtained which, in presence of hydrochloric acid, gave Z_ζ distinctly stronger than the orange samarium band, whilst both bands differ little from those obtained from the original samarium under good experimental conditions. It would seem that there is a close connection between Z_ζ and the so-called abnormal band; both are seen with material rich in samarium and increase in intensity when the three samarium bands tend to diminish.

In yttrium sulphate containing much samarium, the abnormal band has the wave length indicated by Crookes, but in gadolinium, lanthanum, and terbium oxides containing samarium, its position varies between λ 609·1 and λ 612·9.

The line 619·6 observed in a vacuum with a mixture of lanthanum and samariferous gadolinium sulphates seems not to belong to Z_β, because it can be obtained with a mixture of yttria free from Z_β and samaria also free from Z_β.

The addition of hydrochloric acid to an aqueous solution of samarium chloride distinctly increases the intensity of Z_ζ, which becomes well defined at the more refrangible edge and nebulous towards the red, the apparent centre of the band being at λ 614·4 and the more refrangible edge at λ 611·8. Nitric acid has a similar effect on solutions of samarium nitrate, but the band is nebulous at both edges and the apparent middle of the band is at λ 615·5, the more refrangible edge being at λ 614·4 Acetic acid tends to prevent the production of the band Z_ζ, but this influence can to some extent be counteracted by the presence of hydrochloric acid or nitric acid.

Z_β and Z_ζ both increase in intensity in presence of excess of hydrochloric acid, but Z_α is much less affected. Nitric acid, on the other hand, greatly increases the intensity of Z_ζ but has much less effect on Z_β.

An aqueous solution of the chlorides of an earth rich in Z_α and Z_ζ showed Z_α much stronger than Z_β, but when the liquid was mixed with half its volume of hydrochloric acid, Z_β became more intense than Z_α. An aqueous solution of the nitrates of the same earth showed Z_α much stronger than Z_β, but on addition of nitric acid the intensity of Z_β increased, without, however, becoming equal to that of Z_α. On now adding hydrochloric acid, Z_β became more intense than Z_α. The greater the proportion of the earth in the solution of the chlorides or nitrates, the greater seemed to be the intensity of Z_ζ as compared with the orange band of samarium.

C. H. B.

Industrial Preparation of Alumina. By A. Ditte (*Compt. rend.*, **116**, 509—510).—It is customary to treat the aluminous mineral such as bauxite with sodium hydroxide and to mix the aluminate thus obtained with a small quantity of crystallised alumina, such as is obtained by the action of carbonic anhydride on a cold solution of the aluminate. After some hours, practically the whole of the alumina has separated in an easily washed form. This reaction has already been explained by the author (this vol., ii, 278, 279) and the reasons why gelatinous aluminium hydroxide will not produce the same change have been given. The mode of formation explains the freedom of the precipitated alumina from silica, phosphoric acid, &c.

C. H. B.

Preparation of Barium Permanganate. By W. Muthmann (*Ber.*, **26**, 1016—1018).—Potassium permanganate (100 grams) and barium nitrate (140 grams) are dissolved in water (1½ litres), and to the boiling solution barium hydroxide is added in portions of 20 grams until no further evolution of oxygen takes place. The whole is then warmed until the solution has become colourless, the precipitate of barium manganate (containing also some peroxide and carbonate) is collected, washed five times by decantation with 5 litres of boiling water, collected on the filter-pump, washed ten times more with boiling water, suspended in water (1 litre), and carbonic anhydride and superheated steam passed into the mixture for 10 hours. The solution is then filtered twice through an asbestos filter; it contains 65—80 grams of barium permanganate.

From this solution were obtained, by double decomposition, *permanganates of cæsium*, *rubidium*, and *ammonium*, of similar appearance to the potassium salt, with which the first-named is isomorphous. The ammonium salt decomposes into manganese dioxide, water, and nitrogen when its aqueous solution is boiled; when rubbed in a mortar, it explodes, manganese dioxide and ozone being among the products.

C. F. B.

Osmium. By A. Joly and M. Vézes (*Compt. rend.*, **116**, 577—579).—Osmium can easily be fused in the electric arc, and if a current of carbonic anhydride is passed over the metal and the temperature is raised as quickly as possible, there is practically no volatilisation. The metal should be placed in a carbon capsule, as lime is attacked and a fusible compound is formed. Superficial oxidation prevents the precise colour of the metal being determined, but it seems to be bluish-grey, and has a brilliant lustre. The fused metal does not oxidise when exposed to the air at the ordinary temperature; it has a crystalline fracture, and scratches quartz, but is scratched by topaz; sp. gr. 22·48.

Osmium is in many respects similar to ruthenium, and the two form a distinct group like platinum and palladium, or iridium and rhodium. They have almost identical atomic volumes:—

	Atomic weight.	Sp. gr.	Atomic volume.
Ru	101·4	12·06	8·40
Os	190·3	22·48	8·46

C. H. B.

Mineralogical Chemistry.

Stannite from the Black Hills, Dakota. By W. P. Headden (*Amer. J. Sci.*, **45**, 105—110).—The author describes a specimen of stannite from the Peerless Mine in the Black Hills. The appearance of the mass leaves no doubt that it is what remains of an original mass now in an advanced stage of alteration. The pure stannite, free from the accompanying alteration products, gave, on analysis, the following results:—

S.	Sn.	Cu.	Fe.	Zn.	Cd.	Sb.	Insoluble.
28·26	24·08	29·81	7·45	8·71	0·33	trace	1·51

These results agree with the formula heretofore accepted for stannite, except that a small portion of the zinc has been replaced by cadmium. A similar earthy mixture of stannite and its alteration products has been found in the coarsely-grained granite of the Etta Mine. B. H. B.

Hæmatite and Martite Iron Ores in Mexico. By R. T. Hill (*Amer. J. Sci.*, **45**, 111—120).—The iron ores of Mexico have been frequently described, but no attempt has hitherto been made to define their position and origin. The author, therefore, describes in detail the geology of the Monclova ores as a typical locality of the peculiar tertiary Mexican hæmatites, and examines the distribution of similar occurrences in Mexico. The occurrence of large masses of hæmatite in rocks of cretaceous and tertiary age is of great interest, and the Mexican ores of this character, accompanied by martite, have a wide occurrence, which will probably be an important factor in the future iron supply of the world. B. H. B.

Minerals occurring in the Westeregeln Salt-beds. By A. Naupert and W. Wense (*Ber.*, **26**, 873—875).—In the nearly exhausted kainite beds at Westeregeln, lustrous, almost transparent, crystals of another mineral frequently occur, which are readily distinguished from the surrounding kainite, and consist of a new *potassium magnesium sulphate*, $MgSO_4,K_2SO_4,4H_2O$. The same salt is also sometimes found associated with blue rock salt.

The insoluble residue left on extracting carnallite with water, which consists chiefly of anhydrite, contains also small quantities of celestine and kieserite, and a new mineral to which the name *sulphoborite* is given, as it consists of magnesium sulphoborite,

$$3MgSO_4,2Mg_3B_4O_9,12H_2O;$$

it forms distinct, apparently rhombic, crystals, which are for the most part transparent and colourless, but sometimes contain microscopic crystals of ferric oxide. It has the hardness 4, and a sp. gr. of 2·38—2·45. H. G. C.

Anglesite associated with Boléite. By F. A. Genth (*Amer. J. Sci.*, **45**, 32—33).—The mineral described as anglesite by Mallard and Cumenge (Abstr., 1892, 123), associated with boléite from Boléo, Mexico, is found on analysis by the author to have the formula $2PbSO_4 + CaSO_4 + 2H_2O$. He concludes that these so-called anglesite crystals are pseudomorphous after a mineral of the composition $2PbSO_4,CaSO_4$, which has not yet been observed in its original condition, but only after it had taken up $2H_2O$, and changed into gypsum. This now forms a mechanical mixture with the remaining anglesite, from which it can be completely extracted by water. B. H. B.

Native Iron of Ovifak, and the Bitumen in the Crystalline Rocks of Sweden. By Nordenskiöld (*Compt. rend.*, **116**, 677—678; and Berthelot, *ibid.*, 678).—One of the blocks of native iron collected at Ovifak, in Greenland, in 1870 is so hard that it can neither be scratched nor cut, and the author suggests that this may be due to the presence of black diamonds disseminated through the iron.

The bitumens found in the crystalline rocks of Sweden belong to two types, namely, those that yield products of destructive distillation, but leave very little ash, and those that resemble anthracite and yield practically no volatile products but leave a somewhat considerable quantity of ash.

The ash of the anthracitic bitumens contains always, in addition to silica, ferric, calcium, and magnesium oxides, &c., considerable quantities of nickel, uranium, and the cerite and gadolinite earths. This association suggests the possibility of the existence of compounds of carbonic oxide with uranium, cerium, yttrium, &c., analogous to nickel carbonyl.

Berthelot points out that in the writings of Avicenna there is mention of a metallic aërolite, which fell in the Djorjan, in Central Asia, during the 11th century, and which could neither be broken nor worked up. C. H. B.

Sulphur Compounds in Mineral Waters of Barèges. By C. Nicolas (*J. Pharm.* [5], **27**, 128—132).—The waters of Barèges contain sulphur in various forms, such as thiosulphates and thionates, intermediate between sulphates and sulphides, and precipitable, moreover, by cadmium, but not by manganese salts. The sulphur in the various waters was estimated either by precipitation as cadmium sulphide, or by distillation with hydrochloric acid, and oxidation of the distillate with bromine, and was weighed in all cases as barium sulphate. The quantities thus obtained were usually less than those obtained by Dupasquier. Jn. W.

Saline Constituents of Water from the Black Sea. By S. Kolotoff (*J. Russ. Chem Soc.*, **24**, 77—89).—The following numbers were found on analysis of sea-water from different depths at a station in the Black Sea 41° 50′ N. lat., and 9° 20′ E. long. from Pulkova. The depth of water at this station is 976 Russian fathoms.

Depth.	50 fathoms.	100 fathoms.	900 fathoms.
Specific gravity 0°/4°	1·01471	1·01672	1·01746
Solids dried at 180°	1·8262	2·0726	2·1758
Na	0·5582	0·6254	0·6556
K	0·0202	0·0236	0 0298
MgO	0·1129	0·1278	0·1364
CaO	0·0354	0·0400	0·0428
Cl	1·1013	1·1365	1·1915
Br	0·0033	0·0037	0·0039
SO_3	0 1142	0·1297	0·1351
CO_2 in $M''CO_3$	0·0062	0·0072	0·0039
CO_2 in excess	0·0016	0 0010	0·0014
Equiv. acid to 1 equiv. base	0·9903	1·0006	0·9882

J. W.

Physiological Chemistry.

Origin of Fat from Proteïd in the Body. By E. Pflüger (*Pflüger's Archiv*, **51**, 229—320).—In previous papers, the author has advanced the opinion that proteïd, and proteïd alone, is the source of muscular work; and that proteïd is not first transformed into fat or carbohydrate before it is available for this purpose, and that fat or carbohydrate taken as food are of no value in this respect.

Arising out of this is the wider question whether fat can ever originate from proteïd. From the detailed consideration of experiments on metabolic exchange, from the relation of the proportion of fat in milk to that in the blood, from the occurrence of fatty degenerations, and the appearance of adipocere after death, the possibility is rendered a certainty.

The greater part of the present dissertation is of a polemical nature; Voit's older experiments are given at length, and a new interpretation of the facts and statistics deduced therefrom given.

W. D. H.

Nutrition with Carbohydrate and Flesh, and with Carbohydrate alone. By E. Pflüger (*Pfluger's Archiv*, **52**, 239—322).—This paper is a critical account of the older experiments of Pettenkofer and Voit on the subject. The conclusions drawn are that in many cases the decomposition of proteïd will not account for the newly-formed fat, if only starch or starch and flesh are given in the food. Body fat is only formed if a nutritive excess of carbohydrates are present. If this is not the case, the body is overloaded with carbohydrate, not fat. Fat does not appear with great excess of proteïd food if carbohydrate is not given at the same time. After feeding on flesh and starch, or an ordinary mixed diet, the amount of

newly-formed fat does not depend on the quantity of proteïd which undergoes metabolism, but on the excess of carbohydrate. By feeding on carbohydrate alone, fat is seldom formed. W. D. H.

Amount of Albumin required for the Human Body. By L. Breisacher (*Bied. Centr.*, **22**, 203—204; from *Deut. med. Wochenschr.*, 1891, No. 48).—The experiments described bythe author were made on himself. He weighed 52 kilos., was rather free from fat, and not very muscular. For 33 days the food, consisting of meat, rice, potato, bread, eggs, and milk, &c., contained: albumin (68 grams), carbohydrates (494 grams), and fat (60 grams) per diem; his weight remained constant. During the successive three periods of 10 days, the daily amounts of nitrogen in the urine were 8·6, 7·7, and 8·4 grams respectively, so that of the 68 grams of albumin consumed only 52 grams was deposited in the body. The results indicate that for men of average weight (70 kilos.) 87—88 grams of albumin is sufficient; provided, of course, that non-nitrogenous food is consumed in sufficient quantity. N. H. M.

Alcohol as a Substitute for Albumin under various Conditions of Feeding. By C. v. Norden (*Bied. Centr.*, **22**, 204; from *Berl. klin. Wochenschr.*, 1891, No. 23).—Healthy men, after being brought into a condition of nitrogen equilibrium with albumin, fat, and carbohydrates, had certain quantities of alcohol given to them as a substitute for corresponding amounts of fat or carbohydrate. If the albumin-saving power of alcohol is the same as that of carbohydrate and fat, the nitrogen equilibrium should be maintained. In the first experiment, with very nitrogenous food, 65 grams of alcohol so diminished the nitrogen of the urine, that in the first two days 0·7 and 0·9 gram of nitrogen was deposited; on the third, however, and on the fourth day (without alcohol), there was a loss of 1 gram of nitrogen each day. In a second experiment, in which 25—70 grams of alcohol was given for four days, there was a loss of nitrogen of 0·2, 0·8, 1·0, and 1·8 gram, whilst in the next two days (without alcohol) 1·0 gram was lost each day. In the third experiment, a man fed with albumin (50 grams), fat (125 grams), carbohydrates (480 grams), and alcohol (65 grams), lost for eight days an average of 0·3 gram of nitrogen; with a further 65 grams of alcohol and correspondingly less fat, there was, in the one day of the experiment, a deposition of 2·3 grams of nitrogen.

It is concluded that, with richly nitrogenous food, the Calories of alcohol will be well utilised, but not otherwise. N. H. M.

Feeding Experiments with Sunflower Cake, on Cows. By Klein (*Bied. Centr.*, **22**, 175—177; from *D. Landwirth*, 1892, 462 and 468).—Four lots of four Dutch cows were fed as follows:—Maize and potato-distillery liquor (17 litres), dried brewers' grains (1·5 kilos.), linseed cake (0·5 kilo.), meadow hay (2·5 kilos.), chaff (1·5 kilos.), scalded wheat and summer straw (5·0 kilos.), summer straw (2—2·5 kilos.). The total food contained dry matter (12·6 kilos.), digestible albumin, fat, and carbohydrates, 0·96, 0·29, and 5·67 kilos.

respectively. The nutritive ratio was, therefore, 1 : 6·5. For the first week of the experiment this feeding was continued, in the second week the additional food was given in increasing amounts, and in the third and fourth weeks the full amount was given; in the fifth week the amount of additional food was decreased, and in the last two weeks the cows had only the original food. The first group had no additional food, group 2 had 2·05 kilos., group 3, 1·0 kilo. of sunflower meal; group 4 had 4·05 kilos. of linseed and 0·5 kilo. of sunflower cake meal per head daily. With the full amount of extra food, the nutritive ratio was 1 : 5·8 for group 2, 1 : 5·3 for group 3, and 1 : 5·4 for group 4. Having regard to the natural decrease in amount of milk with the advance of the period of lactation, it is calculated that in the third and fourth weeks, there was a daily increase of 0·8 litre per head in group 2, 0·84 litre in group 3, and nearly 0·6 litre in group 4, as a result of the extra food. So that the larger amount of sunflower cake did not give any considerably increased yield over the less. On the whole, sunflower cake seems to be superior to linseed cake in increasing yield of milk. The amount of fat showed great variations, attributed rather to varying composition of the food (especially the distillery liquor) than to the extra food. The unfavourable results are thought to be due to the fact that the original feeding was sufficient without that added for the purpose of experiment. N. H. M.

Influence of Caffeïne and Coffee Distillate on Metabolism. By W. Heerlein (*Pflüger's Archiv*, **52**, 165—185).—The present experiments relate chiefly to gaseous metabolism, a modification of the Regnault-Reiset apparatus being used. The general conclusion drawn is that coffee is neither in itself nutritive, nor does it act as a "sparing" food. It, however, stimulates metabolism, probably by its action on the nervous system. This is especially marked after injections of caffeïne, the amount of oxygen used being always increased. The distillate of coffee smells like coffee; its chief constituent is caffeole, $C_8H_{10}O_2$ (probably methylsaligenin, O. Bernheimer). It has practically no effect on gaseous interchanges. Rabbits were used chiefly in these experiments. W. D. H.

Influence of Ligature of the Bile Duct on Metabolism. By N. P. Krawkow (*Chem. Centr.*, 1893, i, 262—263; from *Wratsch*, 1891, No. 29).—Dogs were dieted to constant weight, and then subjected to inanition. They died after a loss of 35—40 per cent. of their body weight, and this occurred more rapidly if the bile duct had been previously ligatured. W. D. H.

Hydrolytic Ferments. By H. Hildebrandt (*Virchow's Archiv*, **131**, 5—39).—When hydrolytic ferments are introduced into the animal organism, they cause fever. The present experiments, performed with chymosin (rennin), invertin, and emulsin, show further that, locally, they excite positive chemiotaxis. With regard to the fate of hydrolytic ferments in the organism, the experiments were made with emulsin and myrosin, these ferments being foreign to the

animal body. After large doses, administered by subcutaneous injection in rabbits, none was ever found in the urine; but up to six hours after the injection, the administration of amygdalin produced poisoning by hydrocyanic acid. Beyond this time, this did not occur. The question arises, Does the action between ferment and glucoside take place in the blood or in the tissues? It may possibly occur in the blood, as 10 minutes after subcutaneous injection, intravascular injection of amygdalin causes death from hydrocyanic acid poisoning; the same occurs after simultaneously injecting the two substances into different vessels. But as it may also occur when no ferment is discoverable in the blood later on, it probably may occur in the tissues. At the *post-mortem*, ferment is found in the liver in great abundance, and to a less extent in the spleen and pancreas. It is absent from muscle, bile, gastric and intestinal juices, and intestinal walls. It may be found in the liver cells 17 hours after injection, a period when administration of amygdalin produces no result. The ferment is contained in the liver either as an inactive modification or else so that it cannot leave the cells, or it may be that the amygdalin cannot then get into the cells. One has, therefore, to investigate the fate of the injected amygdalin. It appears to be excreted by the kidneys in part. The function of the liver in arresting various poisons is well known. Extracts of the living liver hinder the interaction of emulsin and amygdalin; similar aqueous extracts of dead liver have no such effect. The living liver has a similar hindering action on the action of rennin. The living blood acts similarly, and the change is probably that the ferment is converted into an inactive modification. The injected ferment seems to cause degenerative processes to occur in the liver cells. It also produces other physiological actions, such as stopping the heart in diastole and muscular paralysis.

Aqueous extracts of the fruit of *Syzygium jambolanum* hinder saccharifying actions. Diabetes may be artificially produced by puncture of the medulla, or by phloridzin; or by stimulation of the depressor nerve. In experiments performed under the two latter conditions, extracts of *Syzygium* appeared to have a distinct action in lessening saccharification in the organism. In such experiments, it is necessary that the extracts should be themselves free from sugar, and neutralised, as their original acidity, diminishing the alkalinity of the blood, tends to produce diabetic phenomena.

In conclusion, experiments are recorded which show that, by the administration of successive very small doses of ferments, a certain amount of immunity to larger doses is brought about.

W. D. H.

Synovia and Mucin. By E. Salkowski (*Virchow's Archiv*, **131**, 304—326).—The chief point of interest in connection with synovia is the nature of the mucinoïd substance contained therein.

Mucin from the submaxillary gland was found to contain no phosphorus, or only traces, and readily yielded a reducing substance on treatment with dilute mineral acid. The same is true for paralbumin. Nucleohiston from the thymus contains 2·8 per cent. of phosphorus (Lilienfeld gives 2·4), and yields no reducing substance. Casein contains 0·89 per cent. of phosphorus, and yields no reducing

substance. Vitellin from egg yolk contains 0·95 per cent. of phosphorus, and yields no reducing substance. Mucin from urine contains 1·8 per cent. of phosphorus, and yields no reducing substance; it is, in fact, nucleo-albumin. The synovial mucin is neither true mucin nor nucleo-albumin. It contains no phosphorus, but yields no reducing substance. W. D. H.

Method of estimating the Volume of the Corpuscles of the Blood. By M. Bleibtreu and L. Bleibtreu (*Pflüger's Archiv*, **51**, 151—228).—By estimating the nitrogen by Kjeldahl's method in mixtures of blood and salt solutions, and in the serum of the same blood, data are obtained for calculating the amount of nitrogen in the corpuscles, and thence the proportion of corpuscles in the blood. In the present experiments, horse's blood was used. Mixture with magnesium sulphate solutions gave results in which the proportion of corpuscles is obviously too low. Trustworthy results were obtained by mixing the blood with known volumes of physiological salt solution, which leaves the corpuscles intact. Further, in most experiments, defibrinated blood was used; removal of the fibrin only makes a difference in the percentage of total proteïds in the first decimal place.

The equation obtained is as follows:—

$$(e_1 - e_2)x = \frac{s_2}{b_2}e_2 - \frac{s_1}{b_1}e_1.$$

b_1 and b_2 are the volumes of blood in two mixtures; x is the fraction by which b must be multiplied in order to obtain the volume of liquid in it; s_1 and s_2 are the volumes of salt solution; e_1 and e_2 are the amounts of proteïds in the two mixtures. The volume of the corpuscles $= 1 - x$.

A simpler method consists in taking the specific gravity of the mixtures, and very nearly as good results are obtained: the formula is—

$$x = \frac{s}{b} \times \frac{S - K}{S_0 - S}.$$

Here s = volume of saline solution,
b = volume of blood,
K = sp. gr. of saline solution,
S_0 = „ the serum,
S = „ the mixture.

The matter may be still further simplified by the fact that in the horse the percentage of proteïd in the corpuscles was found to be an almost constant factor (46·85 per cent.), and the corpuscles of almost constant specific gravity; so that in this animal, at least, the formula may be briefly put—

$$V = 2{\cdot}55\ (E - e).$$

Here V = volume of the corpuscles,
E = proteïd in the blood,
e = „ serum.

A rough average of the results obtained shows that the serum contains 7 to 8 per cent. of proteïd; the whole blood 18 to 22.

The volume of the corpuscles per cent. in 10 experiments gave 28·78, 38·8, 26·32, 38·45, 33·04, 39·15, 40·95, 26·14, 37·02, 34·11.

W. D. H.

Volume of Blood Corpuscles. By O. Lange (*Pflüger's Archiv*, **52**, 427—455).—A similar investigation to the preceding, carried out with the blood of the ox and pig. With the blood of the ox, five observations gave 40·05, 35·39, 26·22, 27·37, and 36·95 per cent. of corpuscles per volume. These numbers were obtained by nitrogen analyses. With the blood of the pig, all three methods were employed. By nitrogen analysis, five experiments gave the numbers 30·11, 41·61, 34·38, 41·24, and 43·41. The other methods gave almost the same numbers. The shortened formula for pig's blood is $V = (E - e)\ 2{\cdot}71$. W. D. H.

The Volume and Amount of Proteïd in single Red Blood Corpuscles. By H. Wendelstadt and L. Bleibtreu (*Pflüger's Archiv*, **52**, 323—356).—Having obtained a method of estimating the proportion of corpuscles to fluid per volume in blood (see preceding abstracts), it is a simple extension to combine this with hæmocytometric observations, and thus obtain the volume and amount of proteïd in single red blood corpuscles.

This was done in horse's and pig's blood.

The mean of six observations on horse's and five on pig's blood gave the following results:—

	Horse.	Pig.
Volume of a single red corpuscle ..	0·00000003858 c.c.	0·00000004350 c.c.
Amount of proteïd therein	0·000000018023 mgm.	0·00000001928 mgm.

W. D. H.

Influence of Acids and Alkalis on Defibrinated Blood. By H. J. Hamburger (*Chem. Centr.*, 1893, i, 260—261; from *Du Bois Reymond's Archiv*, 1892, 513—544).—Carbonic anhydride alters the permeability of the red corpuscles, and thus plays an important part in metabolic processes, as in venous blood an exchange between their constituents and the surrounding fluid takes place. This action is not specific to carbonic anhydride, but other acids (hydrochloric and sulphuric) act similarly. The experiments were made with defibrinated blood, but it seems probable that the same is true for the circulating blood. By treatment with acids, the corpuscles yield their proteïd constituents more readily to the serum, and take up chlorides and phosphates from it. Alkali in equivalent quantities produces the opposite effect, and neutralises the action of acid. The susceptibility of the corpuscles to this action is very great, being produced by 0·00775 per cent. of potassium hydroxide and 0·0025 per cent. of hydrochloric acid. W. D. H.

Diastatic Action of the Serum of Blood and Lymph. By M. BIAL (*Pflüger's Archiv*, **52**, 137—156).—A diastatic ferment is present in the serum of blood and of lymph. It is not present in the red corpuscles. It differs from that in saliva, pancreatic juice, and germinating seeds in changing starch into dextrose, not into maltose. The quantity of dextrose obtained is the same, or nearly the same, as that obtained by treating the starch with hydrochloric acid. By submaximal saccharification, dextrin is formed as well. Maltose and achroodextrin are also acted on by this ferment. In the presence of glycerol, starch and achroodextrin were only incompletely converted into dextrose, maltose hardly at all. W. D. H.

Diastatic Ferment in Lymph. By F. RÖHMANN (*Pflüger's Archiv*, 157—164).—In view of the preceding investigation, it became important to discover whether this diastatic ferment exists in the circulating blood and lymph. Injection of starch or glycogen into the circulation and subsequent examination of the urine has led to contradictory results. Injection into a ligatured portion of a vein has the objection that degenerative and coagulative changes may set in, and the presence of sugar in a few minutes is not an absolute proof that living blood contains the ferment. In the present research, glycogen was injected into the lymph, and the lymph from the thoracic duct allowed to flow directly into alcohol. The percentage of sugar in the lymph always rises. Injection of physiological saline solution, the solvent used, does not produce this result.

The diastatic ferment thus proved to be present in lymph can only originate from the blood or the tissues. If the latter is the case, the ferment will pass into the blood from the lymph; a part will pass into the urine; a part remaining in the blood will produce there a saccharifying action. If, on the other hand, the ferment passes into the lymph from the blood, the experiments prove that it is contained in the plasma of the circulating blood. In either case, the dictum of Schiff that "the appearance of a diastatic ferment is the first symptom of the death of the blood" is incorrect. W. D. H.

Glycogen. By S. FRÄNCKEL (*Pflüger's Archiv*, **52**, 125—126).—See this vol., i, 386.

Occurrence of Glycogen in Blood. By G. SALOMON (*Chem. Centr.*, 1893, i, 54—55; from *Centr. physiol.*, **6**, 512—513).—With reference to Huppert's statement that he had discovered glycogen in blood and pus (this vol., ii, 176), the author calls attention to the fact that he had observed the occurrence of glycogen in blood and other animal liquids and effusions as far back as 1877. A. J. G.

Carbamic acid in the Urine after Ingestion of Calcium Hydroxide. By J. J. ABEL and A. MUIRHEAD (*Chem. Centr.*, 1893, i, 261—262; from *Archiv exp. Path. Pharm.*, **31**, 15—29).—Dogs fed on meat free from bone have an acid urine. If from 8 to 10 grams of calcium hydroxide is added to the daily diet, their health remains unimpaired, but the urine is strongly alkaline and ammoniacal.

20 c.c. of such urine yielded 0·00336 gram of ammonia in five days; in another experiment 40 c.c. yielded 0·0074 gram of ammonia in nine days. A deposit of triple phosphate forms in the urine. On the return of the animals to flesh diet, this continues, but the yield of ammonia is not so great. Carbonic anhydride is also given off, and on boiling the urine there is a deposit of calcium carbonate. This is explained on the hypothesis that the urine contains calcium carbamate, which is readily decomposed into calcium carbonate, carbonic anhydride, and ammonia, and confirmed by the separation of calcium carbamate from the urine by Drechsel's method (*Chem. Centr.*, 1891, ii, 713). Experiments on human beings led to the same results.

W. D. H.

Exudations and Transudations. By A. Bernheim (*Virchow's Archiv*, **131**, 274—303).—The analysis of a large number of dropsical fluids is recorded; the sp. gr. and percentage of proteïd being specially noted. An approximation to the percentage of proteïd (E) can be obtained from the sp. gr. (S) by the following formula, $E = \frac{3}{8}(S - 1000) - 2{\cdot}8$. In the case of exudations (inflammatory fluids), the result is not so correct as with transudations (pressure dropsies).

Mere chemical analysis, although valuable as part of a chain of evidence, is not by itself sufficient for a correct diagnosis of the variety or cause of the dropsy under investigation. W. D. H.

Calculus in Muscle. By A. Gascard (*J. Pharm.* [5], **27**, 256—258).—The calculus was found in a fibromuscular sac adhering to the bronchi at the bifurcation of a woman's trachea. It weighed 5·34 grams, and had the following percentage composition:—

Water (after soaking in alcohol)	1·7
Calcium phosphate	68·0
Calcium carbonate	14·2
Organic matter	14·7
Magnesia	trace

Jn. W.

Physiological Action of Cocaïne. By B. Danilewsky (*Pflüger's Archiv*, **51**, 446—454).—In the numerous researches on this subject, attention has been specially directed to the action of cocaïne on sensory nerves. It has, however, also an action in paralysing motor nerves. Langlois and Richet state that the toxic action of cocaïne is proportional to the development of the cerebral system.

In the present research, observations were made on various aquatic animals beloging to the groups of the cœlenterata, echinodermata, worms, arthropoda, and mollusca. A small quantity of cocaïne was added to the water, the concentration of the mixture varying from 1 to 1000—3000.

The general result may be summed up by saying that cocaïne is a protoplasmic poison; it is an anæsthetic to all kinds of animals; and that its action has no relation to the development of the nervous system, still less of a central nervous mechanism. W. D. H.

Resistance of Goats to the Action of Morphine. By L. GUINARD (*Compt. rend.*, **116**, 520—522).—Morphine has no recognisable narcotic influence on goats, and when large doses are administered, death arises chiefly from disturbance of the respiratory functions. The general resistance of goats to the action of the alkaloïd is very remarkable. A young goat weighing 30 kilos. showed little effect beyond a slightly increased cerebral excitability after two doses of 8·0 and 8·5 grams of morphine hydrochloride respectively administered after an interval of 2½ hours by intravenous injection. Two days afterwards, 19·5 grams of the salt, or 0·45 gram per kilo. was administered in the same way at one injection, but after 9 hours the animal seemed to have completely recovered.

The quantity of morphine required to produce death varies considerably with the age and the health of the animal, but is not less than 0·25 to 0·30 gram per kilo. of body weight, or about 1000 times the quantity that suffices to produce narcotism in man when administered in the same way. C. H. B.

Sulphuric acid Poisoning. By E. FRÄNKEL and F. REICHE (*Virchow's Archiv*, **131**, 130—146).—A number of cases of sulphuric acid poisoning are recorded, and references to others given. The chief stress is laid on the kidney affection produced; this is a destruction of the renal epithelium. The glomeruli, vessels, and connective tissue are intact. Albuminuria is not a constant symptom.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Production of Hydrogen Sulphide and Methyl Mercaptan by a Bacterium in Urine. By J. P. KARPLUS (*Virchow's Archiv*, **131**, 210—222).—The urine of a patient with pneumonia and intermittent albuminuria was clear when passed, but in a few hours became cloudy from a bacterial growth, and hydrogen sulphide and methyl mercaptan were given off. This had no relation to the presence or absence of albumin. The bacterium was a short rod, and details regarding its culture and staining properties are given. It does not produce these volatile products when grown in other albuminous fluids. It therefore acts on certain other sulphur-containing constituents of the urine. With sulphates, phenyl potassium sulphate, urinary indican, and thiocyanates, it produces no evolution of hydrogen sulphide; but with thiosulphates there is constantly an evolution of the gas. These salts, however, do not occur to any appreciable extent in normal urine. It must, therefore, be that the source of the gas is those sulphur-containing organic substances to which Salkowski has given the name of "neutral sulphur." This was confirmed by estimating this neutral sulphur before and after the action of the micro-organism. W. D. H.

Fixation of Free Nitrogen by Plants. By T. Schloesing, Jun., and E. Laurent (*Ann. Inst. Pasteur*, **6**, 824—840; compare Abstr., 1892, 1021).—Two new series of experiments are now described; the first was made with higher plants, the second with lower plants. Both were conducted in the apparatus already described (*loc. cit.*). As regards the first series, a subsoil was employed with which a small amount of a mixture of good soils was mixed for the introduction of micro-organisms. After sowing the seeds, the surface of the soil was covered with dry sand to prevent the production of lower plants. Unlike the earlier experiments, considerable amounts of nitrate were added to the soil.

In experiments 1 to 4, 2 kilos. of soil (containing 0·008727 per cent. nitrogen) was employed, in 5, 3 kilos. The amount of ignited sand was 100—200 grams. The experiments were:—(1) check, (2) oats, (3) colza, (4) grasses (*Dactylis*, *Phleum pratense*, *Holcus lanatus*, *Avena elatior* and *fatua*), and (5) potatoes. The direct method was employed only with 1 and 2, and the results were as follows:—Nitrogen employed, 759·3 and 4585·3 c.c.; loss, 0·9 c.c. and 3·0 c.c. The indirect method gave the following results:—Loss or gain: check, −0·7; oats, −2·7; colza, +0·9; grasses, +0·1; and potatoes, −6·5 milligrams of nitrogen. Under the conditions of the experiments, there was, therefore, no fixation of nitrogen.

The experiments with lower vegetation were conducted in the same apparatus, except that instead of the large cylinders, flasks were employed, which were rather less than half filled with soil (600 grams). In experiments 1 and 2, the same soil was employed as in those just described, 100 c.c. of a nutritive solution (without nitrate) was added, and after the introduction of the soil into the flask, 5 c.c. of potassium nitrate solution containing 10 milligrams of nitrogen, and 5 c.c. of soil extract were added. The surface of the soil became covered with algæ, consisting mainly of *Nostoc punctiforme* and *Nostoc minutum*, with some colonies of *Cylindrospermum majus*. There was a considerable fixation of nitrogen (see table), corresponding, in fact, with 60 kilos. per hectare. The amount of organic substance produced was (1) 1·476 and (2) 1·148 gram, and it contained 4·7 and 4·2 per cent. of nitrogen. In experiments 3 and 4, 600 grams of quartz sand, 125 c.c. of nutritive solution, and 5 c.c. of soil extract were employed; no nitrate was given. In 3, a nearly pure cultivation of *Nostoc punctiforme* was produced, in 4, a less pure cultivation of *Nostoc* with colourless masses enclosing bacteria; a colony of *Phormidium papyraceum* and some *Nostoc minutum* were found. Here again, there was considerable fixation. The organic matter found ammounted to 0·827 and 0·543 gram with 4·0 and 5·5 per cent. of nitrogen. Experiments 5 to 8 were made with 600 grams of the soil with the same nutritive solution as before, and nitrate solution containing 14 milligrams of nitrogen. No soil extract was given. No 5. Tufts of *Brachythecium rutabulum* (0·114 gram) and of *Barbuta muralis* (0·172 gram) were planted, samples being kept for nitrogen determination. No. 6. A very small amount of green matter was suspended in water and the water added drop by drop. The resulting growth consisted of *Microcoleus vaginatus* with very small amounts of other Oscillatoria (*Lynghya oscilla-*

toria) and chlorosperms (*Tetraspora*, *Protococcus*, *Stichococcus*, *Alothrix*). Nos. 7 and 8. Check experiments; nothing sown. In 8, the surface of the soil was covered with ignited sand. Two spots of green (*Phormidium autumnale* and *Nostoc punctiforme*) were formed on the surface of the soil in No. 7, whilst in No. 8 (which was covered with ignited sand, but too thinly), a spot of *Phormidium* appeared. Taking, these four experiments together, there was no appreciable fixation of nitrogen. Two more experiments (9 and 10) were made with a moss (*Homalothecium sericeum*) taken from a roof. In 9, the entire moss was employed; in 10, the brown portions only. They were introduced into flasks containing 600 grams of quartz sand with nutritive solution and nitrate. In three weeks, the green portions absorbed about 500 c.c. of carbonic anhydride, but there was no appreciable nitrogen fixation. The following table give the nitrogen results of the whole series.

Nitrogen (milligrams).

Direct method.		Indirect method.				
Initial.	Fixed.	Initial total.*	Final in soil.			Gain or loss.
			Surface.	Interior.	Total.	
c.c.	mgm.					
1. 982·9	65·0	73·5	78·3	57·8	136·1	+62·6
2. 847·1	37·1	73·5	57·1	57·7	114·8	+41·3
3. 1047·0	36·8	1·0	33·2	3·0	36·2	+35·2
4. —	—	1·0	30·4	3·6	34·0	+33·0
5. 1069·5	0·1	68·4	17·0	51·0	68·0	− 0·4
6. 784·8	−0·4	66·4	17·7	48·8	66·5	+ 0·1
7. 740·3	0·6	66·4	—	—	67·5	+ 1·1
8. 580·1	1·8	—	—	—	—	—
9. 1054·1	0·7	—	—	—	—	—
10. 965·7	0·8	—	—	—	—	—

Certain algæ which occur commonly on the surface of soils have therefore, the power of fixing free nitrogen; but, inasmuch as the cultivations of algæ experimented with were not absolutely pure, it cannot be said that certain algæ alone have the power of fixation. It is possible that the algæ effect fixation in symbiosis with bacteria.

N. H. M.

Occurrence of Trehalose in Fungi. By E. Bourquelot (*J. Pharm.* [5], **27**, 113—120).—As previously established (Abstr., 1891, 103; 1892, 519 and 545), the trehalose is probably formed in the vegetative parts of the fungi, and disappears at maturity. In order to ascertain the period at which it is formed, various fungi

* In soil, 52·4 milligrams (Nos. 1 and 2, 5, 6, and 7); as nitrate, 10 milligrams (Nos. 1 and 2), 14 milligrams (Nos. 5, 6, and 7).

were examined at different stages of their growth. *Sclerotinia tuberosa* (Hedw.) gathered in winter contained no trehalose and 0·43 per cent. of mannitol, but at maturity 0·26 per cent. of trehalose and 0·8 per cent. of mannitol, whilst the sporophores then contained only traces of trehalose and 0·79 per cent. of mannitol. The trehalose is formed, therefore, just before fructification. In *Phallus impudicus* (Linn.), the same phenomena were observed. Glucose (0·98 per cent.) was also present; it was slightly reduced in amount (0·77 per cent.) on fructification. In specimens of *Sterigmatocystis nigra* (V. Tiegh.) artificially cultivated, the same phenomena occurred, the trehalose appearing only at fructification, none being formed beforehand or afterwards. JN. W.

Drainage Water from Arable Soils. By P. P. DEHÉRAIN (*Ann. Agron.*, **19**, 65—89).—The Rothamsted experiments have made known the relation between the nitrogen supplied as manure, that recovered in the crop, and that lost in the drainage water, in the case of wheat. But with regard to other crops there is little information. The pot experiments of the author on this subject (Abstr., 1891, 795) are open to the drawback that it is impossible to succeed with some cultures—for example, wheat, sugar-beet, and maize—in pots to the same extent as in the open ground. To remedy this, the author has had 20 water-tight cases made and sunk in the ground, access being made to one side by an excavated path, in order to collect the samples of drainage water which flow from tubes inserted in the sides at the bottom of the cases. Each case is 2 m. square (4 sq. m. surface) by 1 m. in depth, and thus holds 4 cub. m. or about 5 tonnes of soil. They were filled with subsoil and soil as it existed on the spot, and all the cultures succeeded quite as well as in open ground. The results obtained in 1892 are discussed at length. In the annexed table, the results are calculated per hectare.

The season was hot and dry, the rainfall being badly distributed. The drain tubes of the four cases under bare fallow ran on six occasions, namely, July 21, August 31, October 11, 25, November 2, 12. Those of the cases under crop ran only three times, namely, July 21, November 2 and 12. Whenever water was collected, it was measured, and 500 c.c. taken for determination of the nitric nitrogen by Schloesing's method. The loss of nitrates from the bare fallows was considerable in spite of the small rainfall; nitrification in the soil was so active in relation to the rainfall that as much nitrate was lost from the unmanured bare fallow No. 1 as from those manured, Nos. 12, 13, 14. In all cases, the nitrate lost is more or less proportional to the water running through, the richness of the water in nitrates not varying to the extent one would suppose. The crop allowing most loss of nitrate is wheat followed by autumn fallow, and next the beet grown for seed. The sowing of vetches after wheat very strikingly diminishes the autumnal loss of nitrate. Forage maize, potatoes, and sugar-beet allow little loss of nitrate, and the amount recovered in the crop is large. It was remarkable that sugar-beet in these cases succeeded much better than that in the open field plots, the germination in the latter case being affected

Case.	Culture.	Manure per hectare.	Crop per hectare.	Drainage water in mm. of height.	Nitrogen in crop, kilos. per hectare.	N as nitrate in drainage water, kilos. per hectare.	N in drainage water per cent. of N in crop.
1.	Bare fallow	None	—	89·0	—	140·6	—
2.	Rye-grass	None	6000 kilos.	27·7	77·5	19·2	23·5
3.	Sugar-beet	30,000 kilos. f.y.m.	38,250 kilos. roots	14·0	120 in leaves and roots	4·4	3·7
4.	„	30,000 kilos. f.y.m. and 250 kilos. nitrate soda	38,250 „ „	8·0	120	3·2	2·6
5.	„	625 kilos. nitrate and 200 kilos. superphosphate	38,250 „ „	13·7	120	13·0	10·8
6.	Wheat (squarehead)	15,000 kilos. f.y.m.	Grain, 15·75 metric quintals Straw, 37·50 metric quintals	39·7	51·7 grain and straw	54·6	105·5
7.	Wheat followed by autumn vetches	15,000 kilos. f.y.m. and 200 kilos. nitrate	Grain, 17·00 metric quintals Straw, 40·00 metric quintals	16·8	55·5	17·0	30·7
8.	Wheat followed by autumn vetches	500 kilos. nitrate and 200 kilos. superphosphate	Grain, 19·25 metric quintals Straw, 37·50 metric quintals	18·8	59·0	17·9	30·3
9.	Potatoes, Richter's "Imperator"	30,000 kilos. f.y.m.	Tubers, 37,500 kilos.	27·6	162·5	18·2	11·38
10.	„ „ „	30,000 „ f.y.m. and 250 kilos. nitrate	„ 36,500 „	28·7	153·5	16·6	11·03
11.	„ „ „	625 kilos. nitrate and 200 kilos. superphosphate	„ 36,250 „	29·3	157·5	19·7	12·8

Case.	Culture.	Manure per hectare.	Crop per hectare.	Drainage water in mm. of height.	Nitrogen in crop, kilos. per hectare.	N as nitrate in drainage water, kilos. per hectare.	N in drainage water per cent. of N in crop.
12.	Bare fallow	30,000 kilos. f.y.m.	—	97·7	—	121·2	—
13.	„	30,000 kilos. f.y m. and 250 kilos. nitrate	—	102·2	—	156·5	—
14.	„	625 kilos. nitrate and 200 kilos. superphosphate	—	99·2	—	144·8	—
15.	Maize (forage)	30,000 kilos. f.y.m.	Cut green, 77,500 kilos.	16·2	190·0	14·5	7·7
16.	Clover	No manure	Hay, 2750 kilos.	29·7	55·0	25·4	46·1
17.	Oats and clover	No manure	Grain, 24·0 metric quintals; Straw, 27·5 metric quintals	21·7	56·0	31·1	55·6
18.	Beet for seed	30,000 kilos. f.y.m.	Seed, 2134 kilos.	44·2	Not determined	44·8	—
19.	„ „	30,000 „ f.y.m. and 250 kilos. nitrate	„ 2513 „	50·1		46·9	—
20.	„ „	625 kilos. nitrate and 200 kilos. superphosphate	„ 3214 „	42·8		53·3	—

by the drought. The soil of the plots was found to contain 4 and 7 per cent. moisture, that of the cases 10 and 11 per cent.

J. M. H. M.

Influence on Vegetation of the Pressure of Carbonic Anhydride in the Air of Soils. By S. JENTYS (*Ann. Agron.*, **18**, 594—597; from *Bull. Acad. Sci. Cracovie*, July, 1892).—The interstitial air of soils is well known to be much richer in carbonic anhydride than the atmosphere—in soil recently manured, the proportion may reach 10 per cent. The experiments of Boehm appear to show that a large proportion of carbonic anhydride is injurious to plants. The author has re-studied the matter, growing plants in glass pots, and passing in, through a tube inserted in the bottom, air enriched to a known extent with carbonic anhydride. In almost all cases the result of supplying the roots and soil with air containing 4, 5, and 12 per cent. of carbonic anhydride was injurious to the plants experimented on, namely, haricots, rye, lupins. Wheat, however, is an exception. It is possible that plants which do not thrive in recently manured soil are particularly susceptible to this action.

J. M. H. M.

The Organic Constituents of Soils. By BERTHELOT and ANDRÉ (*Compt. rend.*, **116**, 666—672).—After discussing shortly the origin of humus and the causes of the changes which it undergoes, some analyses of Meudon soils are given. The first series of analyses (1—4) were made with a normal loam, the rest with a sandy soil. The following percentage results refer, in the case of carbon and oxygen, to those portions contained in the organic matter of the soil.

	1.	2.	3.	4.	5.	6.	7.	8.
C	19·1	19·8	22·3	43·5	0·82	1·91	1·78	1·118
H	1·5	—	—	—	—	—	—	—
N	1·7	1·0	1·65	1·7	0·093	0·094	0·14	0·14
O	11·9	—	—	—	—	—	—	—

The results obtained with No. 1 correspond with the formula $C_{13\cdot3}H_{12\cdot7}NO_{6\cdot2}$. The analyses 5—8 were made 10 years ago. By means of vegetation, and owing to the fixation of free nitrogen by soil micro-organisms, the sandy soil has been converted into a true vegetable soil. The weight of nitrogen in the soils and sands amounts to 5 and 6 per cent. (in the richest) and 2 and 3 per cent. (in the poorest) of the total organic matter. Natural kaolins were also found to fix free nitrogen to such an extent that it amounted to as much as 7 per cent. of the total organic matter.

As regards the separation of the various organic constituents of soils, very little is, of course, soluble in water. Distilled water was found to dissolve only 0·1 per cent. of the total nitrogen. Cold dilute acid and alkaline solutions dissolve much more, and at the same time give rise to condensations which have been already discussed.

In the course of experiments on the action of alkalis on soils, it was found that (1) 31·2 per cent. of the total organic carbon was insoluble in alkali, (2) 27·1 per cent. was soluble in alkali and repre-

cipitated by acids, and (3) 40·0 per cent. was dissolved by alkali, but was not precipitated by acids. The percentage of nitrogen in these three portions was 4·0, 5·6, and 9·7 respectively.

Another method employed to isolate the organic matter of soils was to extract with cold hydrofluoric and hydrochloric acids; the residue was well washed and dried in a vacuum. Two soils gave the following results.

	1.	2.
Insoluble matter per cent.	2·56	1·46
Carbon of insoluble matter in 100 parts of total	61·5	34·3

The percentage composition of the insoluble matter freed from ash and dried at 100° was

	C.	H.	N.	S.	O.
1	55·32	5·29	4·24	0·84	34·31
2	56·58	5·12	3·04		35·26

The ash (quartz) amounted to (1) 3·52 and 15·58 per cent.

This insoluble substance takes up more or less potash from its solutions, forming two classes of compounds: the one obtained in presence of an excess of potash and rich in alkali, the other by very prolonged washing. Thus 1 gram of the humus, kept for three days with 200 c.c. of 1 per cent. potash, fixed, per cent.,

	1.	2.
K_2O	29·4	29·4

Taking into account the amounts of substance dissolved, it was found that 100 parts of insoluble matter rendered insoluble 44 and 42 parts of potash respectively. The insoluble potash salt when washed until free from alkali contained: Carbon, 61·8 and 61·3; hydrogen, 5·7 and 6·1; nitrogen, 4·6; and potash, 6·2 and 3·7 per cent.

The results showing the absorbent property of soils for potash are analogous to those obtained with artificial humic acid (compare Abstr., 1891, 1089). N. H. M.

Analytical Chemistry.

Origin of Blow-pipe Analysis. By J. Landauer (*Ber.*, **26**, 898—908).—A purely historical paper.

Estimation of Acids by Calcium Carbonate. By C. Friedheim and H. Leo (*Pflüger's Archiv*, **51**, 615—623).—Polemical. A further reply to Wagner's criticisms (compare Abstr., 1891, 1288). W. D. H.

Detection of Chlorine, Bromine, and Iodine in Admixture. By L. F. KEBLER (*J. Anal. Chem.*, **6**, 569—572).—A few drops of nitric acid, sp. gr. 1·42, is added, and the solution warmed gently; it is then cooled, and a few drops of carbon bisulphide added, which will be coloured purple if iodine is present. If the carbon bisulphide only assumes a brownish-yellow tint, bromine is present and iodine absent. If iodine is found, more nitric acid is added, the liquid heated for a few moments and again tested with carbon bisulphide. If the iodine has all been removed, the bromine colour will alone be seen. If bromine is present, more nitric acid is added, and the solution boiled until the bromine is all evolved; the solution is then tested with silver nitrate, when a precipitate soluble in ammonia and insoluble in nitric acid indicates chlorine.

A. J. G.

Estimation of Selenium. By W. MUTHMANN and J. SCHÄFER (*Ber.*, **26**, 1008—1016).—See this vol., ii, 318.

Direct Estimation of Nitrogen in Saltpetre. By A. DEVARDA (*Chem. Zeit.*, **16**, 1952).—The author's process is based on the fact that alkaline solutions of nitrates are reduced by the action of aluminium and zinc powders. Instead, however, of using a mixture of these metals, the author uses an alloy of 45 parts of aluminium, 5 parts of zinc, and 50 parts of copper, which may be readily reduced to powder, and leaves a deposit of metallic copper which will prevent bumping during the subsequent distillation.

The actual process is carried out as follows:—10 grams of the sample is dissolved in a litre of water, and 50 c.c. (= 0·5 gram) is put into a 600 c.c. Erlenmeyer flask and mixed with 60 c.c. of water, 5 c.c. of alcohol, and 40 c.c. of aqueous potash (sp. gr. 1·3). About 2·5 grams of the powdered alloy is added, and the flask is at once connected with a condenser, the end of which dips into the standard acid, at least during the earlier part of the distillation, which may be started after the mixture has been kept at a gentle heat for about half an hour. The process cannot be used in presence of nitrogenous organic matter. If ammonium salts are present, the free ammonia must be first distilled off before adding the reducing alloy. The test analyses prove the great accuracy of the process. L. DE K.

Estimation of Nitrogen in Urine. By C. ARNOLD and K. WEDEMEYER (*Pflüger's Archiv*, **52**, 590—591).—By using, in Kjeldahl's process, a mixture of 3 parts of sulphuric acid and 1 part of potassium sulphate (Gunning gives 2 : 1, *Zeit. anal. Chem.*, **28**), and adding 1 gram of mercury and copper sulphate during the distillation (Arnold, *Arch. Pharm.*, 1885, 5), 10 c.c. of urine being used, the distillation is complete in 30 to 40 minutes, and the estimation can be completed in an hour. This method is thus considerably quicker than the Schneider-Seegen soda-lime method. It gives rather higher results, but these are considered to be more correct. W. D. H.

Estimation of Organic Nitrogen. By A. PETIT and L. MONFET (*J. Pharm.* [5], **27**, 297—300).—The nitrogen is converted into

ammonium sulphate by fuming sulphuric acid and mercury, then liberated from this combination by alkaline hypobromite, and measured in the usual way. The process is especially applicable to the determination of the total nitrogen in urine. The acid (5 c.c.) is added drop by drop to the urine (10 c.c.) in a conical flask, the acid liquid brought to the boil, a globule of mercury added, and the boiling continued until the liquid is completely decolorised. This is effected in 15—30 minutes, the longer interval being necessary if albumin is present. After cooling, water (20 c.c.) is gradually added, and then strong aqueous soda, until the acid is nearly neutralised, the temperature not being allowed to rise. The whole is then made up to a definite volume (50 c.c.), and an aliquot portion (10 c.c.) treated with alkaline hypobromite (20 c.c., 35 per cent. of bromine) in a graduated tube in the usual manner, and the volume of nitrogen read off. Trial determinations made with alkaloïds, which require, however a much longer time than the less stable compounds, accord very excellently with theory. JN. W.

Gasometric Estimation of Nitrites by means of Schäffer's Reaction. By C. M. VAN DEVENTER (*Ber.*, **26**, 958—959).—In a previous paper in connection with this method (this vol., ii, 298), it was stated that about 5 per cent. of the volume of liquid must be added to the volume of nitric oxide. Further experiments indicate, however, that the necessary correction is 3 per cent. The solubility of nitric oxide, which for water is about 5 per cent., is lowered by the presence of salts. The permanganate method gives results about 0·5 per cent. too low on the dissolved nitrite; this the author believes to be due to unavoidable loss of nitrous acid by volatilisation.

A. R. L.

Valuation of Basic Slag. By O. FOERSTER (*Chem. Zeit.*, **16**, 1596—1597).—The author states that a really trustworthy process for the estimation of the available amount of phosphoric acid in basic slag is still a desideratum. The best results are obtained when the sample is boiled with dilute sulphuric acid, and the resulting liquid treated according to the molybdate method. L. DE K.

Estimation of Potassium by the Lindo-Gladding Process. By A. F. HOLLEMAN (*Chem. Zeit.*, **16**, 1920—1921).—This process consists in evaporating the solution containing the potassium compound with platinic chloride, the excess of which is then removed with alcohol. In order to remove sulphates, the residue is washed with a strong solution of ammonium chloride, which is in turn removed by washing with alcohol (80 per cent. by vol.). The potassium platinochloride is then dried and weighed. Breyer and Schweitzer, having tried the process, give it as their opinion that it leads to erroneous results. The author, however, states that, if properly conducted, the process is perfectly trustworthy. L. DE K.

Separation of Calcium and Magnesium from Zinc as Phosphates. By G. C. STONE (*J. Anal. Chem.*, **6**, 516—518).—The separation depends on the solubility of zinc phosphate in a mixture of

ammonia and ammonium chloride (strong ammonia, 700 c.c.; ammonium chloride, 100 grams, made up to 1 litre). The cold solution, containing calcium, magnesium, and zinc, is nearly neutralised with ammonia, and 50 c.c. of the ammonia solution and 1 c.c. of a 10 per cent. phosphate solution added for every 0·1 gram of zinc supposed to be present. The precipitate is allowed to settle, filtered, and washed three times with dilute ammonia (1 : 8). The precipitate is dissolved in hydrochloric acid, a little phosphate solution added, and again precipitated with 25 c.c. of the ammonia solution, the precipitate being collected and washed as before. The filtrates and washings are then combined, nearly neutralised with nitric or sulphuric acid, rendered slightly acid with acetic acid, and heated at about 80° until the precipitate crystallises; this is then collected, washed well with hot water, dried, ignited, and weighed as $Zn_2P_2O_7$. If there are but mere traces of calcium and magnesium, one precipitation is sufficient, but two are required if more than 3 or 4 milligrams are present. The amount of ammonia solution used should be proportional to the amounts of these metals; with small amounts, less than the quantities given above will suffice, but with larger amounts it is advisable to use more than 25 c.c. for the second precipitation.

The method is not well adapted for separating very small amounts of zinc from calcium and magnesium, although the results are very satisfactory where the reverse is the case: in the first case, probably the best method would be to precipitate the zinc as sulphide, and then dissolve the precipitate and treat as above. A. J. G.

Estimation of Copper by Volhard's Thiocyanate Method. By R. Henriques (*Chem. Zeit.*, **16**, 1597—1598).—This estimation is performed as follows. The copper solution is mixed first with sulphurous acid, and then with a definite quantity of solution of potassium thiocyanate, which should of course be added in excess. After making up to a definite bulk, the liquid is filtered through a dry filter, and an aliquot part of the filtrate is acidified with nitric acid, mixed with ferric sulphate, and the excess of the thiocyanate is titrated back with standard solution of silver nitrate.

The author has, however, not succeeded in getting even approximately correct results, which is not to be wondered at, seeing that a solution of a thiocyanate cannot be acidified with nitric acid without being rapidly decomposed. The process may, however be trusted to give good results if the filtrate is first mixed with excess of silver nitrate, then acidified with nitric acid, and then titrated back with standard solution of thiocyanate with ferric sulphate as indicator.

L. de K.

Estimation of Mercury in Dilute Solutions of Mercuric Chloride. By L. Vignon (*Compt. rend.*, **116**, 584—586).—Mercury can readily be estimated gravimetrically in the form of sulphide in solutions containing not less than 1 part of mercuric chloride in 1000. 50 c.c. of the solution is mixed with 5 c.c. of pure hydrochloric acid of 22° and 10 c.c. of a clear saturated solution of hydrogen sulphide. Under these conditions, the precipitate forms rapidly, and is easily filtered and washed.

In more dilute solutions, the metal is most readily estimated colorimetrically by adding hydrogen sulphide solution to a known volume of the liquid, and comparing the depth of the brown tint with that produced by mercuric chloride solutions of known strength. Within somewhat wide limits, the intensity of the coloration is simply proportional to the quantity of the mercuric salt present, and a distinct coloration is obtained with 100 c.c. of a solution containing 1 part of mercuric chloride in 240,000 parts of water. C. H. B.

Separation of Iron Oxide from Alumina in Phosphatic Rocks by Fusion with an Alkali Carbonate. By C. GLASER (*J. Anal. Chem.*, **6**, 524—526).—The author finds that his process as previously described may give erroneous results when the iron is in excess of the aluminium, but very accurate results are obtained by the following modification.

The hydrochloric acid solution of a phosphorite is nearly neutralised with ammonia, using methyl-orange as indicator, ammonium acetate is added until the colour changes completely from red to pale yellow, and the mixture is then heated on the water bath at a temperature not exceeding 70° until the iron and aluminium phosphates are completely separated. The precipitate is collected, and thoroughly washed with water (not above 70°) by aid of a filter pump. As slight amounts of calcium salts are likely to be retained mechanically, it is advisable to redissolve and precipitate again in the manner described above, first, however, adding a little sodium phosphate to the solution. The mixed phosphates are then heated in a tared platinum crucible, care being taken, however, that the temperature is not high enough to fuse the ferric phosphate. When incineration of the filter is completed, the mass is weighed, then covered with pure sodium carbonate, fused for about 10 minutes over a blast lamp, allowed to cool, and the crucible then placed in a beaker containing a little water. After the melt is moistened, the beaker is heated until the water boils. The cake can now be easily removed from the crucible and transferred to the boiling water without loss. The contents of the beaker are boiled until everything but the ferric oxide is dissolved, then filtered hot, and the residue washed with boiling water. The ferric oxide on the filter, and any that may have adhered to the crucible, is now dissolved in hydrochloric acid, and the iron estimated by precipitation with ammonia in the usual way. To the filtrate from the fusion, which contains everything but the iron, hydrochloric acid is added to expel carbonic anhydride, and the aluminium is then precipitated as phosphate by the addition of ammonium acetate. A. J. G.

Investigation of Potable Water by Schäffer's Nitrite Reaction. By C. M. VAN DEVENTER and B. H. JÜRGENS (*Ber.*, **26**, 932—939; compare this vol., ii, 298).—Schäffer has stated that when a few drops of potassium ferrocyanide solution and acetic acid are added to water containing so small a quantity as 1 part in 617,000 of potassium nitrite, a yellow colour is produced, due to the formation of potassium ferricyanide. A solution containing nitrates gives the same

reaction after being heated with lead raspings. The authors confirm these observations.

Making use of the reaction as a test for nitrites in water, it is found that the results are vitiated by the oxygen of air as well as by that dissolved in the water, as the nitric oxide produced in the reaction is thereby oxidised to nitrous anhydride or nitric peroxide, which interact with a further quantity of ferrocyanide. The same objection may be brought against the iodide of starch method; indeed Thresh (Trans., 1890, 185) avails himself of the latter test for the estimation of dissolved oxygen in water. Instead of the apparatus employed by Thresh, the authors keep the water from contact with the air by pouring upon its surface a thin layer of petroleum; this method serves also for Schäffer's test.

To 1 litre of water containing potassium nitrite (0·0006 gram), petroleum was added, and subsequently potassium ferrocyanide (0·1 gram), and about 1 gram of acetic acid; the colourless solution gradually became yellow, the intensity of the coloration being constant at the end of 15 minutes, whilst water containing no nitrite did not exhibit a distinct yellow coloration until the lapse of two hours. Water containing iron, lead, and zinc is boiled with sodium carbonate, and the cooled filtrate tested. Schäffer's test is not less sensitive than the iodide of starch test; it is less influenced than the latter by the presence of hydrogen peroxide. Nitrates have no influence on either process, and the effect of nitric acid is small. A. R. L.

Estimation of the Hardness of Water by means of Soap. By G. BUCHNER (*Chem. Zeit.*, **16**, 1954).—The author calls attention to the fact that, in order to get trustworthy results, the temperature of the water should be exactly 15°. At a higher temperature, a very much larger amount of the soap solution will be required.

L. DE K.

Estimation of Ammonium Thiocyanate in Nitrogenous Manures. By P. L. JUMEAU (*J. Pharm.* [5], **27**, 190—193).—A specimen of commercial ammonium sulphate having been found to exercise an injurious influence on vegetation, was examined for thiocyanates, of the ammonium salt of which it proved to contain as much as 9 per cent.

In the presence of chlorides, the sulphates having been removed, the thiocyanates may be estimated by oxidation with potassium permanganate and hydrochloric acid, and precipitation as barium sulphate. In the absence of chlorides, they may be titrated with silver nitrate, using ferric sulphate as an indicator. In the presence of both cyanides and chlorides, they may be titrated with potassium permanganate in the presence of sulphuric acid, the permanganate being standardised against a solution of ammonium thiocyanate of known strength. JN. W.

Distillation of Mixtures of Water and Alcohol. By E. SOREL (*Compt. rend.*, **116**, 693—695).—The tables compiled for the purpose of determining the composition of a mixture of water and alcohol from the composition of the vapours that it evolves differ con-

siderably amongst themselves. Direct experiment shows that the cooling effect of the walls of the retort or still exerts an important disturbing influence, the liquid that trickles down the inner surface of the still containing, as a rule, twice as much alcohol as is present in the boiling liquid.

Experiments made with a retort which was kept at a uniform temperature over the whole of its surface, lead to the construction of the following table, which is intended to replace the older table of Gröning. The strength of the liquid and the distillate are given in Gay-Lussac degrees at 15°.

Boiling liquid.	Vapour.	Boiling liquid.	Vapour.
0°	0°	55°	76·54°
5	35·75°	60	78·17
10	51·00	65	79·92
15	61·50	70	81·85
20	66·20	75	84·10
25	67·95	80	86·49
30	69·26	85	89·05
35	70·60	90	91·80
40	71·95	95	95·05
45	73·45	97·6	97·60
50	74·95		

C. H. B.

Estimation of Sodium Sulphide, Sulphite, and Thiosulphate in Glycerol from Soap Works. By C. Ferrier (*Chem. Zeit.*, **16**, 1840).—Glycerol recovered from soap-lyes generally contains from 8 to 10 per cent. of chlorides or sulphates, which seriously affects its commercial value. Should it also contain alkali sulphides, sulphites, or thiosulphates, it becomes an almost useless article. It is, therefore, important for a manufacturer to ascertain their presence and also their quantity. The author now recommends the following process:—

50 grams of the crude sample is diluted with boiled water, neutralised with hydrochloric acid, and made up to 500 c.c. The solution is heated to 60—70° and treated with a few grams of animal charcoal, or better still, with the carbonaceous mass obtained as a bye-product in the manufacture of potassium ferrocyanide, which must, however, be purified by treatment with nitric acid, and by subsequent calcination in a closed crucible. The solution must then be filtered and tested as follows:—

The author uses as test solutions (1) normal iodine solution; (2) a solution of lead nitrate, prepared by dissolving 13·3 grams of normal lead carbonate in a sufficiency of dilute nitric acid, neutralising the excess of acid by means of sodium carbonate, and diluting to 1 litre; (3) an alkaline lead solution prepared by dissolving the same amount of lead carbonate in nitric acid, adding aqueous potash until the precipitated lead hydroxide has dissolved, and making up to 1 litre. 1 c.c. of these lead solutions contains 0·0103 gram of lead, corresponding with 0·0039 gram of sodium sulphide. Before attempting to make a quantitative estimation, it is as well to make

a few qualitative tests. To test for a sulphide, a drop of the solution is put on a paper drenched with lead nitrate. If no coloured spot is formed, the sample contains less than 0·01 per cent. of sulphide. A still more delicate test consists in pouring some of the solution into a flask and mixing it with a few drops of hydrochloric acid and a pinch of sodium hydrogen carbonate. The liquid is then boiled and the vapour allowed to act on a filter-paper moistened with lead nitrate. Even when the sample contains only 0·001 per cent. of sulphide, a yellow stain is formed.

To test for sulphites and thiosulphates, a little of the glycerol solution is mixed with a few drops of solution of barium chloride, which precipitates any carbonate, sulphate, or sulphite. After filtering, the liquid is mixed with a few drops of hydrochloric acid and potassium permanganate. The presence of even 0·01 per cent. of thiosulphate will cause a decided turbidity. To prove the presence of sulphites, the barium precipitate is well washed with boiling water and then suspended in starch solution. A few drops of weak iodine solution are now added, which will cause a very transient blue colour should sulphites be present.

To estimate the sulphides, the lead nitrate solution is added to 25 c.c. of the glycerol solution until precipitation ceases. To see whether enough lead has been added, a drop of the supernatant fluid is put on to lead nitrate paper. The liquid is filtered and mixed with a pinch of sodium hydrogen carbonate and a few drops of starch solution. Iodine solution is now run in until a permanent blue coloration is obtained. This will give the joint amount of sulphites, thiosulphates, and other reducing salts. Another 25 c.c. of the solution is now mixed with the proper amount of lead nitrate, and then with 3 c.c. of a strong solution of strontium chloride. This will cause the precipitation of any carbonates, sulphates, and sulphites, and any thiosulphate will remain in solution, and may be titrated by means of iodine. The difference between the two titrations will give the amount of sulphites. If the sample is free from other reducing agents, such as cyanides, nitrites, or ferrous compounds, the operation would be ended; but as this is never certain, a third titration must be made as follows:—Another 25 c.c. of the sample is mixed with the requisite amount of the alkaline lead solution, filtered, and, after adding 2 c.c. of pure hydrochloric acid, heated to 100°. After cooling, the liquid is neutralised with sodium carbonate, any sulphurous acid is precipitated with strontium chloride, and any iodine now absorbed will represent the other reducing agents, and must be allowed for when calculating the amount of the thiosulphate.

As regards the purification of the glycerol, the author recommends addition of calcium hypochlorite in quantity just sufficient to convert any sulphide, sulphite, or thiosulphate into the more harmless sulphate.

L. DE K.

Detection of Small Quantities of Sugar in Urine. By J. SEEGEN (*Chem. Centr.*, 1893, i, 136—137; from *Pharm. Centrhalle*, **33**, 730—731).—The urine is filtered through blood charcoal until completely decolorised. The charcoal is then washed on the filter with distilled water. The charcoal retains colouring matters, uric acid, and

those constituents of the urine which interfere with the separation of the cuprous oxide, so that now the reduction can be observed, not as a yellow coloration, but by the actual separation of the oxide. The washing with water removes some of the sugar retained by the charcoal, so that the second and third wash waters are, practically, aqueous sugar solutions, in which Fehling's solution will detect very minute amounts of sugar. Icteric urine is not decolorised by the use of a layer of blood-charcoal 5—6 cm. high to 20—40 c.c. of urine, but other, even strongly-coloured urines are decolorised by passing twice through the charcoal. Untreated urine containing 0·1—0·5 per cent. of sugar decolorises Fehling's solution without giving any precipitate; after passing through animal charcoal, the liquid gives a yellow turbidity when warmed with Fehling, but the second and third washings of the charcoal give a red precipitate of cuprous oxide. With only 0·05—0·1 per cent. of sugar, a cloudiness is only obtained in the filtrate and the first washings after a little time ($\frac{1}{2}$—1 minute), whilst the second and third wash-waters do not give any reaction. With still less sugar, it is frequently 10—15 minutes before a reaction occurs, when white flocks of separated phosphates first separate, and on these some yellow points appear; after a time, the whole liquid is coloured yellow.

Urines containing much urates must be strongly acidified with hydrochloric acid, put aside for 24 hours, neutralised, and then treated as above. As normal urine does not give any indication by this test, the occurrence of a reaction must be held to show an amount of sugar above the normal. A. J. G.

Solubility of Rosin Oil and Mineral Oils, and Mixtures thereof, in Acetone. By E. Wiederhold (*J. pr. Chem.* [2], **47**, 394—397; compare Demski and Morawski, Abstr., 1886, 282).—Whilst rosin oil is soluble in acetone in nearly all proportions, mineral oils are either insoluble or only very sparingly soluble. In order that this difference may be available for purposes of evaluation, the acetone must be perfectly dry and free from acid; the presence of aldehyde is not of material importance. All the samples of rosin oil which the author has examined dissolve to a clear solution in half their volume of such acetone at 15°, but only in considerably more if the solvent be not dry. In this connection, the liability of such volatile liquids to condense moisture from the air by the cold of their own evaporation must be remembered, and all vessels containing them must be well stoppered.

The solubility of petroleum in acetone appears to be some sort of function of the specific gravity. Thus for a clear solution at 15°, 1 vol. of burning oil of sp. gr. 0·830 required 4 vols. of acetone; 1 vol. of Russian spindle oil of sp. gr. 0·898 required 40—41 vols.; 1 vol. of "oleonaphtha" of sp. gr. 0·908 required 70—71 vols.

2 c.c. of the sample of oil is shaken with 20 c.c. of acetone at 15° in a cylinder graduated in $\frac{1}{10}$ c.c., and the mixture is allowed to separate for 12—24 hours; under these conditions, a quantity of the oil will be left undissolved, depending on the specific nature of the oil, and varying in the case of Russian lubricating oils from 1·7 c.c. to

0·8 c.c.; the American cylinder oils remain almost entirely insoluble. A table gives the quantities left undissolved in the case of nine Russian oils examined by the author. For thick and unrefined oils, it is necessary to warm the cylinder. The presence of rosin oil in the sample will be detected by the quantity left undissolved being smaller than is normal for an oil of the same designation and gravity. Thus, in the case of an "oleonaphtha" of sp. gr. 0·906, which consisted of Russian spindle oil whose sp. gr. had been raised to that of oleonaphtha by admixture of $\frac{1}{5}$th of its weight of rosin oil, there was left only 1 c.c. after 2 c.c. had been shaken with 20 c.c. of acetone, whereas genuine oleonaphtha leaves 1·5 c.c.

The test is only trustworthy in the absence of free acids. The author detects free acid in an oil by shaking it with cuprous oxide, and observing if it be coloured green after a lapse of 12 hours.

A. G. B.

Qualitative and Quantitative Wax Analysis. By H. Röttger (*Chem. Zeit.*, **16**, 1837—1839).—The author, who has tried every published method for the detection of adulteration of wax, has come to the conclusion that the only trustworthy method is the one recommended by Hübl. This process consists in taking the acidity and the saponification figures, which for pure wax are fairly constant, whilst they differ very much when such substances as tallow, stearic acid, rosin, or paraffins have been added.

The difference between the acidity and saponification figures is called the ether number. The figures for pure wax are: acidity, 20; ether, 75; saponification, 95; and the ratio of the first two is 3·75. For Japan wax, the latter figure is 10; for tallow, 44; for rosin, 0·015; for paraffins, 0, &c., so that a serious adulteration may be detected without the least difficulty.

Benedikt and Mangold take the acidity number of the sample as usual, then saponify another portion with strong aqueous potash, liberate the fatty acids with hydrochloric acid, and, after removing any trace of the latter by repeated boiling with water, they take the acidity number again and call it the saponification figure. The author cannot recommend this modification of the process, as the percentage of wax found in adulterated samples was considerably too high.

L. de K.

Hübl's Process for testing Wax. By G. Buchner (*Chem. Zeit.*, **16**, 1922).—This process practically consists of the taking of the acidity and saponification numbers, and is rightly considered to be a safe and elegant method. The author, however, recommends boiling with excess of normal alcoholic potash for at least one hour; otherwise the saponification will not be complete, and the result will be quite untrustworthy.

L. de K.

Detection of Foreign Fats in Wool Fat. By H. Helbing and F. W. Passmore (*Chem. Centr.*, 1893, i, 142; from *Pharm. Zeit.*, **37**, 704, 712—713).—Wool fat, a cholesterol fat, cannot be saponified by aqueous potash, but is readily saponified by heating at 100° in a

closed vessel with alcoholic potash. The saponification number of lanolin determined in this manner is found to be 83·44. As this is only about one-half of that of ordinary fats, the determination of the saponification number can be applied to the detection of foreign fats in lanolin; paraffins and other hydrocarbons are found in the unsaponified portion, and can be estimated as usual. All the other wool fats, after deduction of the potash value of the free fatty acids contained in them, yield the same saponification number as lanolin. Test analyses are quoted, mixtures of lanolin with oils, fats, and hydrocarbons, and the results appear to be fairly satisfactory.

A. J. G.

Estimation of Indigotin in Commercial Indigo. By O. MILLER (*J. Russ. Chem. Soc.*, **24**, 275—299).—The water in a fair sample of indigo is determined by heating at 100° to constant weight. To estimate the indigotin, a weighed portion (0·5 gram) is thoroughly mixed in a porcelain basin with 10 grams of hydrogen sulphate, H_2SO_4, not oil of vitriol, and heated on the water-bath for an hour with occasional stirring. In this way all the indigotin is converted into the disulphonic acid, which is then dissolved in water and made up to a litre. 50 c.c. of this solution is diluted with 600 c.c. of water, and titrated with standard potassium permanganate (about 1/280 normal), the colour changing from blue to green, olive, dirty yellow, and finally to a golden-yellow. The disappearance of the olive tint marks the end of the reaction. Pure indigotin gives a pure orange-yellow solution; commercial indigo gives oxidised solutions with either a brownish or reddish tint. The oxidation takes place according to the equation

$$5C_{16}H_{10}N_2O_2 + 4KMnO_4 + 6H_2SO_4 = 5C_{16}H_{10}N_2O_4 + 2K_2SO_4 + 4MnSO_4 + 6H_2O.$$

As indigotin is more readily oxidised, under the conditions of experiment, than indigo-brown, the presence of the latter does not materially interfere with the estimation. Gums, resins, carbohydrates, and albumin, even when added to commercial indigo in quantity, do not appreciably affect the accuracy of the method.

J. W.

Estimation of Theïne in Tea. By N. V. SOKOLOFF (*J. Russ. Chem. Soc.*, **24**, 130).—The method adopted by the author for the estimation of the amount of theïne in tea differs from that ordinarily employed in that, instead of an aqueous extract, a sample of the tea itself is taken, the moisture having been previously ascertained. The tea is moistened with 15—20 drops of alcoholic ammonia, and extracted in a Soxhlet apparatus with chloroform. Subsequently, the chloroform is distilled off, and magnesia added to the residue, which is then extracted three times with boiling water, filtered, and the filtrate evaporated to dryness. The theïne remaining is slightly yellow. To purify it, the aqueous solution is extracted with chloroform, on evaporation of which the theïne is obtained quite colourless.

J. W.

General and Physical Chemistry.

Optical Properties of Liquid Oxygen. By K. Olszewski and A. Witkowski (*Chem. Centr.*, 1893, i, 595; from *Naturwiss. Rundschau*, **8**, 75).—The index of refraction of liquid oxygen is deduced by the authors from the angle of total reflection by means of an apparatus which is described. The relative refractive index of liquid oxygen is thus found to be 1·2232 and the absolute coefficient 1·2235, a value agreeing well with that obtained by Liveing and Dewar, namely, 1·2236. The absorptive power of a column of liquid oxygen of 1 mm. thickness between λ 577 and λ 570, that is, the most intense portion of the yellowish-green absorption band of liquid oxygen, was found to be between 84 and 89 per cent.; whilst for the red absorption band between λ 630 and λ 638, a mean value of 88 per cent. was obtained. A. R. L.

Refraction Constants of Phosphorus in the Free State, and in its Compounds with Elements or Monovalent Groups. By F. Zecchini (*Gazzetta*, **23**, i, 97—109).—The author has determined the refraction constants of a number of phosphorus compounds with respect to the line D; the data obtained are summarised in the following table.

Substance.	Temperature.	$P\frac{\mu_D - 1}{d}$.	$P\frac{\mu_D^2 - 1}{d(\mu_D^2 + 2)}$.	Atomic refraction of phosphorus.	
				From n.	From n^2.
PEt_3	18·6°	67·55	40·24	17·24	9·47
PEt_3,EtI.....	20·0	110·42	65·44	18·24	10·29
PCl_5 (1)	26·1	64·70	37·77	14·45	7·71
PCl_5 (2)	24·4	66·91	38·80	16·65	8·81
$POCl_3$ (1).....	25·1	42·41	25·25	8·92	4·97
$POCl_3$ (2).....	26·6	42·39	25·24	9·60	5·74
PBr_3.....	26·6	66·03	36·50	20·01	9·72
PI_2 (1)	29·3	74·60	38·13	24·12	9·92
PI_2 (2)	24·0	75·03	38·19		

The atomic refractions given under the headings n and n^2 are calculated from the molecular refractions, $P\frac{\mu-1}{d}$ and $P\frac{\mu^2-1}{(\mu^2+2)d}$ respectively; the values employed in calculating from the simpler formula are those previously given by the author (this vol., ii, 253), whilst Conrady's values are used in working from the theoretical formula. Triethylphosphine, phosphorus tribromide, and phosphorus oxychloride were examined in the pure state; triethylphosphonium iodide was employed in a 14·6034 per cent. aqueous solution, whilst,

with phosphorus pentachloride, determinations (1) and (2) were made with 6·5171 and 6·0775 per cent. carbon bisulphide solutions respectively. In boiling carbon bisulphide, phosphorus diiodide has a molecular weight corresponding with the formula P_2I_4; carbon bisulphide solutions containing (1) 7·1896 and (2) 6·3215 per cent. of the iodide were used in the determinations.

The author concludes that the atomic refraction of phosphorus varies very considerably with the nature and number of the other elements with which it is combined; the value is least in the chlorides of phosphorus and greatest in the iodide, the value deduced from the bromide being intermediate. Hydrogen phosphide gives a much lower value for the atomic refraction of phosphorus than do the halogen compounds of the same type. Compounds of phosphorus with the same elements give practically the same values for the atomic refraction; this is especially well shown with the tri- and pentachlorides. The very low refraction equivalent of phosphorus oxychloride is remarkable; it gives the atomic refraction of phosphorus as less than half that which the element has in the free state or when combined with chlorine alone. It is noteworthy that with these compounds the formula $\frac{P\mu-1}{d}$ gives as a rule more consistent results than the theoretical formula. W. J. P.

Refraction Constants of the Acids of Phosphorus and their Sodium Salts. By F. Zecchini (*Gazzetta*, **23**, i, 109—120; compare preceding abstract).—The author has measured the refraction constants, with reference to the D-line, of phosphoric, metaphosphoric, pyrophosphoric, phosphorous, and hypophosphorus acids, and their sodium salts in aqueous solution. The atomic refraction of phosphorus deduced from the molecular refraction of the sodium salts cannot be entirely depended on, owing to the arbitrary values which must be assigned to the metal; the numbers obtained from the refractive indices of the acids are given in the following table, together with Thorpe and Tutton's value for phosphorous oxide (Trans., 1890, 545).

	Atomic refraction of phosphorus obtained from formula.	
	n.	n^2.
P_4O_6	9·71	5·33
HPO_3.....	5·94	2·77
H_3PO_4	4·08	1·46
H_3PO_3	5·18	2·46

It is noteworthy that a much higher value for the atomic refraction is obtained from the oxide than from the acids or salts.

W. J. P.

Influence of Temperature on the Rotatory Power of Liquids. By A. Aignan (*Compt. rend.*, **116**, 725—727).—The author points out that where a liquid is optically inactive because it is a mixture of

two active substances of opposite rotatory powers, the inactivity will, as a rule, hold only for rays of a certain wave-length, and the mixture will be active in one direction for rays of shorter wave-length and active in the opposite direction for rays of greater wave-length. This phenomenon is well shown by mixtures of lævogyrate terebenthene and dextrogyrate camphene.

Similarly a change in the temperature of such liquids will disturb the optical equilibrium, and the liquid will become active in one direction when the temperature rises and in the other when the temperature falls. This phenomenon also is observed with the mixture of terebenthene and camphene, and with red rays the rotatory power changes in sign between 61° and 73°, and with yellow rays between 13° and 33°, whilst with green rays the liquid is always dextrogyrate between 13° and 90°, but the rotatory power increases with the temperature.

Phenomena of this kind were observed by Biot in the case of solutions of tartaric acid. The author suggests that the liquids examined by Colson (this vol., ii, 255) are mixtures of two substances of opposite optical activities, and that the variations observed in the rotatory power are due to the causes specified above. C. H. B.

Meidinger's Cells. By A. A. Krakau (*J. Russ. Chem. Soc.*, **24**, 325—330).—The author undertook an investigation of cells of the Meidinger type used in telegraphic practice with a view to ascertain which form was most suitable, and to study the E.M.F., efficiency, &c., of each. He found, however, great variations in the results obtained with precisely similar elements, so that he was unable to arrive at any definite conclusions, except that unknown secondary reactions play a very important part in the working of the elements. J. W.

Leclanché Battery. By A. Ditte (*Compt. rend.*, **116**, 812—815).—When a couple formed of a rod of zinc and a plate of platinum is immersed in a 10 per cent. solution of sodium chloride, the zinc becomes covered with a layer of zinc hydroxide, which, at some distance down the rod, spreads out and forms a kind of diaphragm, which separates the liquid into two parts of different composition, the upper section being strongly alkaline and containing no zinc, whilst the lower is neutral and contains zinc chloride.

Since the heat of formation of zinc oxide is greater than that of water, the zinc decomposes the water, but the action is at once arrested by the formation of a superficial film of zinc oxide, insoluble in water or a solution of sodium chloride. The decomposition of sodium chloride solution by the zinc platinum couple is also exothermic, and zinc chloride and sodium hydroxide are formed. The dilute solutions of the latter being lighter than the salt solution, there is an upward current of sodium hydroxide solution along the surface of the platinum plate, and a downward current of zinc chloride solution from the zinc rod. The zinc hydroxide is formed by the interdiffusion of these two currents.

If the platinum plate is replaced by a mass of manganese peroxide,

polarisation is greatly reduced, and the layer of liquid which the current has to traverse is also much thinner; consequently, the action is more rapid and the phenomena are more marked. In the ordinary battery, the sodium hydroxide solution is retained in the porous cell, and no zinc hydroxide is formed in the outer liquid until the alkaline solution escapes. C. H. B.

Abnormal Electromotive Forces of Mercury. By H. Brandenburg (*Zeit. physikal. Chem.*, **11**, 552—576).—The electromotive force of an element of the type Zn | H_2SO_4 | Hg is greatly diminished by the addition of a few drops of potassium iodide solution to the liquid. Potassium bromide and chloride exercise the same influence in a less degree, whilst potassium sulphide reduces the difference of potential from 1·4 to about 0·2 volt. The author has investigated a large number of substances with regard to this property, and finds the following salts show it to a greater or less extent: potassium sulphide, cyanide, thioacetate, selenocyanate, thiocyanate, chloride, bromide, iodide, nitrite, ferrocyanide, and sodium selenothiosulphate, thioglycollate, thiosulphate, thiophenolate, and sodium succinimide. The action of these substances is due to their removing mercury ions, which are present in the sulphuric acid in small quantity, either by forming insoluble compounds with them, or by producing double salts, from which mercury is not dissociated as an ion. J. W.

Electrical Conductivity of Mixtures. By D. Konovaloff (*J. Russ. Chem. Soc.*, **24**, 440—450).—The author has determined the electrical conductivity of mixtures of weak bases, such as aniline, with weak acids, such as acetic acid. The bases investigated were aniline, methylaniline, dimethylaniline, and toluidine; the acids were acetic, propionic, and butyric. Measurements were made at 21°, and, in the case of mixtures of aniline with acetic acid, also at 16°. The results are given in tables and in a series of curves made by tabulating the percentage composition of the mixture as abscissa against the electrical conductivity as ordinate. For each pair of substances, the conductivity starts from the neighbourhood of zero for the pure amine, rises to a maximum as acid is added, and then diminishes to zero again for the pure acid. The composition of the mixture, expressed as molecules of amine in 100 mols. of mixture, which gives the maximum conductivity at 21°, is exhibited in the following table, as well as the maximum value in mercury units multiplied by 10^8.

Base.	Acid.	Composition.	Maximum value.
Aniline	Acetic.....	14·0	27·0
Methylaniline...	„	14·3	28·7
Toluidine.....	„	14·0	18·4
Dimethylaniline.	„	12·0	22·1
Aniline.....	Propionic...	31·0	6·7
„	Butyric.....	35·0	1·0

J. W.

Electrical Conductivities of Phosphoric acid and of Alkali Phosphates. By D. BERTHELOT (*Ann. Chim. Phys.* [6], **28**, 5—28).—This paper contains the author's measurements of the electrical conductivities of phosphoric acid and of sodium, potassium, and ammonium mono-, di-, and tri-phosphates. The conclusions deduced from the results as to the basicity of phosphoric acid have been already given (Abstr., 1892, 395). A. R. L.

A small Air Thermometer for Laboratory Use. By L. MEYER (*Ber.* **26**, 1047—1051).—A modification of the apparatus devised by Bottomley (*Phil. Mag.* [5], **26**, 149). J. B. T.

Melting Point Determinations. By E. HAASE (*Ber.*, **26**, 1052—1054).—The melting points of the following substances were determined by the air thermometer described by L. Meyer (preceding abstract). The freezing mixture employed consisted of solid carbonic anhydride and anhydrous ether; the lowest temperature observed was −75—78°. Chlorobenzene, −44·9°; bromobenzene, −31·1°; iodobenzene, −29·8°; orthochlorotoluene, −34°; metachlorotoluene, −47·8°; parachlorotoluene, +7·4°; orthobromotoluene, −25·9°; metabromotoluene, −39·8°; parabromotoluene, +28·2°; chloroform, −62°; trichloronitromethane, −64°; ethylenic chloride, −42°; benzylic chloride, −48°; trichlorotoluene, −22·5°; benzaldehyde, −26°; zinc methide, −40°; zinc ethide, −28°; titanium chloride, −25°; arsenic chloride, −16°.

The following substances become visicid and turbid at −75°:—methylic valerate, ethylic valerate, propylic valerate, amylic normal butyrate. The following substances are clear, but more or less viscid, at the same temperature: amylic formate, amylic acetate, amylic valerate, isobutylic formate, isobutylic acetate, ethylic normal butyrate, methylic propionate, and ethylic propionate; methoxybenzene and ethoxybenzene are gelatinous. Methylic formate, propylic formate, methylic acetate, ethylic acetate, propylic acetate, ethylic chloride, ethylidenic chloride, ethylidenic chlorobromide, methylic bromide, trimethylenic bromide, carbon oxychloride, silicon tetrachloride, and sulphur monochloride are unaltered at −75°.

J. B. T.

Thermochemistry of the Ions. By W. OSTWALD (*Zeit. physikal. Chem.*, **11**, 501—514).—From the electromotive force of cells into which various metals enter, and from Thomsen's thermochemical data, the author calculates the following "heats of ionisation," that is, the heat change on the conversion of free metal into metallic ions.

	Atom.	Equivalent.
Potassium	+ 61·0 Cal.	+61·0 Cal.
Sodium	+ 56·3 „	+56·3 „
Lithium	+ 62·0 „	+62·0 „
Strontium	+115·5 „	+57·8 „
Calcium	+107·0 „	+53·5 „
Magnesium	+106·7 „	+53·4 „
Aluminium	+117·5 „	+39·2 „

	Atom.	Equivalent.
Manganese	+ 48·1 Cal.	+24·0 Cal.
Iron (ferrous ions)	+ 20·0 „	+10·0 „
„ (ferrous into ferric)	− 12·1 „	−12·1 „
Cobalt	+ 14·6 „	+ 7·3 „
Nickel	+ 13·5 „	+ 6·8 „
Zinc	+ 32·6 „	+16·3 „
Cadmium	+ 16·2 „	+ 8·1 „
Copper (cupric ions)	− 17·5 „	− 8·8 „
„ (cuprous ions)	− 17·0 „ (?)	−17·0 „
Mercury	− 20·5 „	−20·5 „
Silver	− 26·2 „	−26·2 „
Thallium	+ 1·0 „	+ 1·0 „
Lead	− 1·0 „	− 0·5 „
Tin	+ 2·0 „	+ 1·0 „

All the metals that easily form ions have positive heats of ionisation; the others have negative heats of ionisation. J. W.

Thermochemistry of α-Dibromopropicnic acid. By S. Tanatar (*J. Russ. Chem. Soc.*, **24**, 365—371).—Heat of solution of α-dibromoproprionic acid at 13° = 1·64 Cal.

Heat of neutralisation with potash at 14—16° = 14·85 Cal. There is no thermal effect when the normal potassium salt of α-dibromopropionic acid is mixed with excess of dilute alkali or excess of the dilute acid.

There is an evolution of 0·464 Cal. when equivalent quantities of decinormal solutions of potassium chloride and α-dibromopropionic acid are mixed, and an absorption of 0·544 Cal. when equivalents of hydrogen chloride and potassium α-dibromopropionate are taken. The heat effect if either acid completely displaced the other from its salts would be 1·106 Cal., evolution in the one case and absorption in the other.

The heat of dissolution of the salt $KC_3H_3Br_2O_2 + H_2O$ at 14° is −2·878 Cal., and of the anhydrous salt +0·518 Cal., so that the heat of hydration is +3·396. The heat of dissolution of the acid salt $KC_6H_7Br_4O_4$ is −7·91 Cal.

The heat of neutralisation of propionic acid with potash is +13·46 Cal.; its heat of dissolution, +0·604 Cal.; and that of its potassium salt, +2·74 Cal. J. W.

Thermochemical Investigation of Ureïdes derived from Acids containing 1 and 2 Carbon Atoms. By C. Matignon (*Ann. Chim. Phys.* [6], **28**, 70—125).—The general mode of procedure adopted in this and subsequently published memoirs (following abstracts) is to determine the heats of combustion of the compounds by means of the calorimetric bomb and deduce from these data their heats of formation.

The heat of neutralisation of carbamide by nitric acid is very small and indicates that the nitrate is almost completely dissociated; in a concentration corresponding to $\frac{1}{24}$ mol. per litre, the value is *nil*,

whilst in a concentration of $\frac{1}{8}$ mol. per litre it is +0·13 Cal. When carbamide nitrate ($\frac{1}{8}$ mol.) is dissolved in water (1 litre), an absorption of 10·7 Cal. is observed. The heats of dissolution of solid carbamide (−3·6 Cal.) and of solid nitric acid (+6·6 Cal.), lead to the relation:—HNO_3 sol. + CON_2H_4 sol. = CON_2H_4,HNO_3 sol. .... +13·8 Cal. This value is much smaller than those corresponding with the most feeble inorganic bases. Aniline is a much stronger base; its solution, saturated with nitric acid, should give +7·4 Cal., whilst carbamide only furnishes +0·2 Cal.

Ethylcarbamide. Heat of combustion at constant volume, +471·9 Cal., and at constant pressure, +472·2 Cal. Heat of formation:—C_3 diamond + O + N_2 gas + H_8 gas = CON_2H_3Et sol. .... +86·7 Cal. The heat of dissolution of ethylcarbamide at 14° in a concentration of $\frac{1}{24}$ per litre is −2·3 Cal. The difference in the heats of combustion of carbamide and of ethylcarbamide is +320·7 Cal., a value abnormally large. The formation of ethylcarbamide from liquid alcohol and solid carbamide develops +3·8 Cal.

Thiocarbamide. Heat of combustion at constant volume, +341·9 Cal., and at constant pressure, +342·8 Cal. Heat of formation, +30·5 Cal. Heat of dissolution at 10° in a concentration of $\frac{1}{2}$ equivalent per litre, −5·33 Cal. The displacement of sulphur by oxygen in thiocarbamide develops +50·3 Cal. The heat of neutralisation of thiocarbamide by nitric acid at 11° in a concentration of $\frac{1}{4}$ mol. per litre of water is +0·02 Cal. (carbamide gives +0·24 Cal). Heat of dissolution of thiocarbamide nitrate is −8·5 Cal. HNO_3 sol. + CSN_2H_4 sol. = CSN_2H_4,HNO_3 sol. .... +9·8 Cal. The displacement of oxygen by sulphur in carbamide diminishes the basic function, and it would appear from this that sulphur is more negative than oxygen; thiocarbamide has, however, no acidic function, its heat of dissolution in water and potash being identical.

Ammonium thiocyanate. Heat of combustion at constant volume, +344 Cal., and at constant pressure, +345 Cal. Heat of formation, +28·4 Cal. The transformation of this compound into thiocarbamide develops +2·1 Cal.

Guanidine and its Salts (Abstr., 1892, 1142).

Ureïdes of Normal Acids (Abstr., 1891, 1448).

Ureïdes of Mono- and Poly-basic Acids containing 2 Carbon Atoms.—Hydantoïn:—Heat of combustion at constant volume, +312·4 Cal., and at constant pressure, +311·9 Cal. Heat of formation, +109 Cal. The formation of hydantoïn from glycollic acid and carbamide develops +5·6 Cal. Heat of dissolution in water at 11° in a concentration of $\frac{1}{25}$ mol. per litre is −6·1 Cal., or in potash, +0·5 Cal. Carbamide glycollate is obtained in the form of white crystals, insoluble in ether, by evaporating mixed solutions of carbamide and glycollic acid. Its heat of dissolution in water at 17° in a concentration of $\frac{1}{10}$ mol. per litre is −8·2 Cal. De Forcrand gives −2·8 Cal. as the heat of dissolution of glycollic acid; consequently $C_2H_4O_3$ sol. + CON_2H_4 sol. = $CON_2H_4,C_2H_4O_3$ sol. .... +2 Cal. Heat of formation of carbamide glycollate, −243·4 Cal. The formation of hydantoïn from carbamide glycollate:—$CON_2H_4,C_2H_4O_3$ sol. = $C_3H_4N_2O_2$ sol. + $2H_2O$ .... + 3·6 Cal.

Carbamide combines with glycocine with scarcely any appreciable development of heat, and the product, *carbamide amidoacetate*, forms large, lustrous crystals, and completely dissociates in water. Its heat of dissolution at 12° in a concentration of $\frac{1}{33}$ mol. per litre is −6·4 Cal.; consequently:—CON_2H_4 sol. + $C_2H_5NO_2$ sol. $CON_2H_4,C_2H_5NO_2$ sol. .... +0·8 Cal. The direct formation of hydantoïn from carbamide amidoacetate would involve the absorption of −14·6 Cal.

Hydantoïc acid.—Heat of combustion at constant volume, +308·9 Cal., and at constant pressure, +308·4 Cal. Heat of formation, +181·6 Cal. It is a monobasic acid. Heat of dissolution in potash, +6·8 Cal.; excess of potash does not alter this value. The heat of dissolution in water is about −6·5 Cal., so that the heat of neutralisation of the dissolved acid must be about +13 Cal., the ordinary value observed with monobasic acids. The conversion of hydantoïn into hydantoïc acid:—$C_3H_4N_2O_2$ sol. + H_2O sol. = $C_3H_6N_2O_3$ sol. develops +2·2 Cal. In the presence of potash:—$C_3H_4N_2O_2$ diss. + KOH diss. = $C_3H_5KN_2O_3$, develops 8·8 Cal.

Allantoïn (Abstr., 1891, 1448). Methylallantoïn. Heat of combustion at constant volume, +567·7 Cal., and at constant pressure, +566·9 Cal. Heat of formation, +180·6 Cal. The difference between the heats of combustion of allantoïn and methylallantoïn (+153·1 Cal.) is normal.

Ureïdes of Oxalic acid.—Parabanic and Oxaluric acids (Abstr., 1891, 1449). Oxamic acid. Heat of combustion at constant volume, +129·5 Cal., and at constant pressure, +128·8 Cal. Heat of formation, +163·3 Cal.

Dimethylparabanic acid. Heat of combustion at constant volume, +539·1 Cal., and at constant pressure, +538·6 Cal. Heat of formation, +139·9 Cal. The difference between the heats of combustion of dimethylparabanic and of parabanic acids, +326 Cal., gives +163 Cal. as the difference for each methyl group, a value abnormally large.

A. R. L.

Thermochemical Investigation of Polybasic Ureïdes and of Uric acid. By C. Matignon (*Ann. Chim. Phys.* [6], 289—394).—When alloxantin is heated on the water-bath with sulphuric acid, and an equal volume of water added, a yellowish compound separates which, on boiling with water, is converted into a mixture of parabanic and barbituric acids (Finck, *Annalen*, **132**, 304). This compound is *oxalylmalonic diureïde*, $C_7H_4N_4O_5$. Barbituric acid (malonic ureïde). Heat of combustion at constant volume, +354·2 Cal., and at constant pressure, +353·4 Cal. Heat of formation, +161·8 Cal. Grimaux has synthesised the acid by heating together malonic acid and carbamide:—$C_3H_4O_4$ sol. + CON_2H_4 sol. = $C_4H_4N_2O_3$ sol. + $2H_2O$ .... +8·2 Cal. The formation of barbituric acid is considerably more exothermic than that of the oxalic ureïdes, the syntheses of which have not been effected. Acid malonic ureïde, $C_3H_4O_4,CON_2H_4$, is obtained in colourless, anhydrous crystals when a solution of malonic acid and carbamide is allowed to evaporate over sulphuric acid. The heat of combustion at constant volume is +357·2 Cal., and at constant pressure, +356·3 Cal. Heat of formation, +296·9 Cal. Its forma-

tion from solid malonic acid and solid carbamide develops +2·5 Cal. It decomposes into barbituric acid and water:—$C_3H_4O_4,CON_2H_4$ sol. = $C_4H_4N_2O_3$ sol. + $2H_2O$ sol. .... +5·7 Cal. A neutral malonic ureïde could not be prepared. Barbituric acid has two acidic functions, of which the first is stronger than that of the normal carboxylic acids and of the same order as that of picric acid; whilst the second acidic function is very feeble, more so than the third function of phosphoric acid; the corresponding salts are decomposed by water.

Alloxan (Abstr., 1891, 1448). The heat of combustion of mesoxalic acid at constant volume is +129·4 Cal., and at constant pressure, +128·3 Cal.; the heat of formation is +292·7 Cal. The formation of alloxan from the acid and carbamide (solid) develops +1·2 Cal. Dialuric acid (tartronic ureïde), $CO<^{NH\cdot CO}_{NH\cdot CO}>CH\cdot OH$, oxidises so rapidly in the air that no constant values could be obtained with it. The heat of combustion of tartronic acid at constant volume is +166·6 Cal., and at constant pressure, +165·8 Cal. The heat of formation is +165·8 Cal. The formation of dialuric acid from carbamide and tartronic acid (solid) would develop +4·2 Cal.; its heat of formation is +201·1 Cal. (approx.). Uramile (amidomalonic ureïde), $CO<^{NH\cdot CO}_{NH\cdot CO}>CH\cdot NH_2$. Heat of combustion at constant volume, +380 Cal., and at constant pressure, +379 Cal. Heat of formation, +170·7 Cal. Thionuric acid, $CO<^{NH\cdot CO}_{NH\cdot CO}>CH\cdot NH\cdot SO_3H$, was discovered by Liebig and Wöhler. It is partially hydrolysed in aqueous solution into uramile, but may be obtained in acicular crystals by evaporating its aqueous solution over concentrated sulphuric acid. Its aqueous solution causes a brisk evolution of hydrogen on the addition of zinc or cadmium, and decomposes carbonates in the cold. The author describes at length its mon- and di-acid salts; they are crystalline compounds which rapidly become red in the air.

Alloxantin (Abstr., 1891, 1448). Amalic acid (tetramethylalloxantin). Heat of combustion at constant volume, +1241·9 Cal., and at constant pressure, +1240·6 Cal. Heat of formation, +374 Cal. Hydurilic acid, $C_8H_6N_4O_6$ (*Ber.*, **9**, 1102). Heat of combustion at constant volume, +660·5 Cal., and at constant pressure, +658·5 Cal. Heat of formation, 302·9 Cal. Baeyer regards this compound as a diureïde resulting from the combination of barbituric and dialuric acids. The interaction of the solid acids would develop +10·3 Cal., and the author has effected the synthesis of hydurilic acid by heating together barbituric and dialuric acids.

Deoxyamalic acid is best prepared by heating amalic acid in a sealed tube at 180—185° for three hours. Its heat of combustion at constant volume is +1322·6 Cal., and at constant pressure, +1321·8 Cal. Heat of formation, +292·8 Cal. The difference between the heats of combustion of deoxyamalic acid and amalic acid indicates that the latter is the dihydroxy-derivative of the former. Murexide. Heat of combustion at constant volume, +738·8 Cal., and at constant pressure, +736·7 Cal.

Uric acid. Heat of combustion at constant volume, +462·7 Cal., and at constant pressure, 461·4 Cal. (see also Stohmann, Abstr., 1892, 6). Heat of formation, +148·1 Cal. The oxidation of uric acid in the animal organism has been shown by numerous observers to be incomplete. The various hypotheses claiming to explain the formation of uric acid in the animal organism are then discussed at length; thermic measurements of the salts of uric acid are also given. Pseudouric acid. Heat of combustion at constant volume, +455·2 Cal., and at constant pressure, +454 Cal. Heat of formation, +224·5 Cal. The transformation of pseudouric acid into uric acid (solid compounds) is endothermic (−6 Cal.). Isouric acid. Heat of combustion at constant volume, +460·6 Cal., and at constant pressure, +459·4 Cal. Heat of formation, +150·1 Cal. The transformation of uric acid into isouric acid (solid compounds) would give rise to the development of +2 Cal., a value too small to enable the change to be actually effected.

Theobromine. Heat of combustion at constant volume, +846·45 Cal., and at constant pressure, +846 Cal. Heat of formation, +90·1 Cal. Caffeïne. Heat of combustion at constant volume, +1016·5 Cal., and at constant pressure, +1016 Cal. Heat of formation, +83·4 Cal. Since the introduction of a methyl group, combined with nitrogen, raises the heat of combustion of a compound about +165 Cal. (see next abstract), this value has been calculated for xanthine from those given above for caffeïne and theobromine. The heat of combustion of xanthine is thus found to be +518·5 Cal., and its heat of formation +91 Cal.

Thiohydantoïn. Heat of combustion at constant volume, +502·4 Cal., and at constant pressure, +503 Cal. Heat of formation, +58·9 Cal. Thiohydantoïc acid. Heat of combustion at constant volume, +497·9 Cal., and at constant pressure, +498·5 Cal. Heat of formation, +132·4 Cal. A. R. L.

General Results of the Thermochemical Study of the Ureïdes. By C. Matignon (*Ann. Chim. Phys.* [6], **28**, 498—528).—The fact that the heat of combustion of orthotoluidine is approximately the same as that of metatoluidine, whilst that of methylaniline is greater, led Petit (*Ann. Chim. Phys.* [6], **18**, 145) to conclude that the introduction of a methyl group into the side chain is a less exothermic phenomenon than the introduction of such a group into the benzene nucleus. The author's results confirm this. He compares the heats of combustion (given in the preceding abstracts) of certain ureïdes, and finds that the displacement by methyl of an atom of hydrogen combined with nitrogen raises the heat of combustion of the compound by 164—165 Cal., whilst the displacement by methyl of an atom of hydrogen combined with carbon raises the heat of combustion at most 157 Cal. The primary amines have a lower heat of combustion than the secondary or tertiary amines isomeric with them. The heat of combustion of the residue $= CH_2$:—C (diamond) + H_2 gas + O_3 = CO_2 + H_2O .... + 163·3 Cal., leads to the conclusion that the heat of formation of a compound is increased by 6—7 Cal. when methyl is substituted for one of the hydrogen atoms combined

with carbon, and is diminished by 1—2 Cal. when one of its hydrogen atoms in combination with nitrogen is displaced by methyl.

The above law indicates that metameric compounds exist which present notable differences in their heats of formation, and it renders possible, in many cases, the molecular migration of alkyl groups in combination with nitrogen to a carbon atom. It can, therefore, be used to establish the constitution of a compound.

Nitroguanidine has a heat of combustion at constant volume +211·4 Cal.; and at constant pressure +210·3 Cal. The heat of formation is +22 Cal. A study of this compound indicates that the formation of nitro-derivatives is less exothermic when the nitro-group enters into combination with a nitrogen atom; it is, therefore, to be expected that such nitro-derivatives will be the more powerful explosives.

The introduction of an alkyl group into a compound seems to diminish the positive work necessary to effect its dissolution.

The research has led to the deduction of certain rules, which will serve for the synthesis of new ureïdes. A. R. L.

Graphical Treatment of some Thermodynamical Problems on Conditions of Equilibrium in Salt Solutions with Solid Phases. By A. C. van Rijn van Alkemade (*Zeit. physikal. Chem.*, **11**, 289—327).—An application of the thermodynamical principles of Gibbs to the consideration of some special cases of conditions of equilibrium in salt solutions. H. C.

Determination of the Specific Gravity of Salts Soluble in Water. By J. W. Retgers (*Zeit. physikal. Chem.*, **11**, 328—344).—In determining the specific gravity of salts soluble in water, the author has formerly employed, with advantage, the method of suspension in liquids so adjusted, that their specific gravities equal those of the salts taken. As only few liquids have hitherto been found available for the above purpose, attention has now been devoted to obtaining new liquids of high specific gravity for use in the determinations. In the first place, attempts were made by dissolving various metallic iodides in methylenic iodide to effect an increase in the specific gravity, 3·324 at 16°, of this liquid. Only in three cases was an appreciable increase noticed, these being with stannic iodide, 3·481 at 10°, with arsenious iodide, 3·449 at 12°, and with antimonious iodide, 3·453 at 12°. A mixture of stannic and arsenious iodides, dissolved in methylenic iodide, gave a liquid of specific gravity 3·610 at 12°, and by using a mixture of stannic and antimonious iodides a specific gravity of 3·63 was obtained. Experiments were then made with arsenic tribromide, a compound melting at 20° to a nearly colourless liquid of specific gravity 3·540 at 25°. By dissolving trihaloïds of antimony and bismuth in this, heavier liquids were obtained, the highest observed specific gravity being 3·80 in the case of a mixture of arsenious and antimonious iodides in arsenious bromide; this liquid solidifies, however, at 31°. By mixing solutions of arsenious and antimonious iodides in arsenious bromide with those in methylenic iodide, a liquid was obtained of specific gravity 3·702,

which only solidifies at 20°; it has, however, the disadvantage of being opaque. A liquid which does not solidify at the ordinary temperature, and was the heaviest observed fulfilling this condition, was obtained by mixing stannic iodide and arsenious bromide. The specific gravity is 3·731 at 15°, but the solution is opaque. H. C.

Dissociation of Saline Hydrates and Analogous Compounds. By H. Lescœur (*Ann. Chim. Phys.* [6], **28**, 237—256).—A continuation of the author's researches on this subject (Abstr., 1889, 815; *Ann. Chim. Phys.* [6], **19**, 35, 533; **21**, 511; **25**, 423). The compounds examined in this memoir are the so-called acid acetates; they include additive compounds of sodium, potassium, lithium, and thallium acetate with acetic acid, and of sodium and potassium trichloracetate with acetic acid. They are analogous to saline hydrates, being formed by direct addition of acetic acid. They lose acetic acid at the ordinary temperature by a phenomenon analogous to efflorescence, but unlike the saline hydrates, which do not effloresce when their tension of dissociation is lower than that of the atmospheric aqueous vapour, the acid acetates lose acetic acid in the atmosphere, whatever be their tension of dissociation. This is because the atmosphere does not contain acetic acid vapour, as it does aqueous vapour, which limits the dissociation of the hydrates. A. R. L.

Determination of the Electrolytic Dissociation of Salts by means of Solubility Experiments. By S. Arrhenius (*Zeit. physikal. Chem.*, **11**, 391—402).—The discrepancy observed by Noyes between the numbers obtained for the degree of dissociation of dissolved salts from his solubility experiments (Abstr., 1892, 1143), and those derived from the electrical conductivities, and more especially the opinion which this investigator has expressed, that the former series of numbers is more trustworthy than the latter, and that water takes a part in the electrolysis of a salt solution, has induced the author to submit this question to an experimental examination. He finds that the electrolytic dissociation, calculated from the solubility, differs enormously in the case of the same salt, for example, silver nitrate, according to whether the sparingly soluble salt with which this is combined is more or less soluble. No agreement, therefore, can be obtained between numbers which apply to one and the same salt, so that solubility experiments do not give trustworthy results for the determination of the electrolytic dissociation. The cause of this is, seemingly, that the law of mass action, upon which the calculation of the experimental results is based, is not applicable to strongly dissociated electrolytes. H. C.

Electrolytic Dissociation of Water. By J. J. A. Wijs (*Zeit. physikal. Chem.*, **11**, 492—494).—Methylic acetate and water react to form methyl alcohol and acetic acid (or an acetate) at a rate proportional to the number of hydrogen ions or hydroxyl ions present in the solution. The reaction conditioned by the hydroxyl ions (saponification by a base) proceeds much more rapidly than that conditioned by the hydrogen ions (catalysis by an acid). Water behaves both as a weak base and also as a weak acid, so that it is assumed to be slightly

dissociated into hydrogen ions and hydroxyl ions $H_2O = \overset{+}{H} + \overset{-}{OH}$. To measure the extent of this dissociation, the author prepared an aqueous solution of methylic acetate, carefully sterilised and freed from acid impurity, and from time to time titrated it with standard alkali in order to ascertain the amount of acetic acid liberated. The action was supposed to be caused entirely by the hydroxyl ions, and only the first few titrations were considered, as the free acetic acid contributes a considerable number of hydrogen ions as the decomposition proceeds. From the rate of decomposition, it appeared as if the water were a $0{\cdot}1 \times 10^{-7}$ normal solution of hydroxyl ions, that is, that water is to this extent dissociated under the conditions of experiment. (See next abstract.) J. W.

Electrolytic Dissociation of Water. By W. Ostwald (*Zeit. physikal. Chem.*, **11**, 521—528). From the electromotive force of a gas cell consisting of two electrodes saturated with hydrogen, one immersed in a solution of alkali and the other in a solution of acid, it is possible to calculate the concentration (osmotic pressure) of the hydrogen ions in the alkaline solution, and of the hydroxyl ions in the acid solution. The concentration of these ions in pure water may then be calculated. It follows from the electromotive force actually ascertained (about 0·7 volt) that the concentration of the hydroxyl (and hydrogen ions) in water is $0{\cdot}9 \times 10^{-6}$. (Compare preceding abstract.) J. W.

Electrolytic Dissociation of Acid Salts. By A. A. Noyes (*Zeit. physikal. Chem.*, **11**, 495—500).—The author shows that for the acid salt of a weak bibasic acid, H_2A, the following relation holds good:—

$$ck = (k + m)md^2,$$

when k is the dissociation constant of the free acid, c the dissociation constant of the acid ion $\overset{-}{HA}$, m the concentration of the salt, and d the ratio of the concentration of the hydrogen ions to m.

Trevor's results (*Zeit. physikal. Chem.*, **10**, 32) are found to be in general harmony with this equation. J. W.

The Freezing Points of Sodium Chloride Solutions. By S. U. Pickering (*Ber.*, **26**, 1221—1227).—The author has critically examined, both by the graphic and mathematical methods, the values obtained by Jones (this vol., ii, 263), and finds that they show the presence of the breaks mentioned by him even more clearly than his own results do. Two parabolas deduced from the results so as to recognise the breaks agree perfectly with the ascertained experimental error, whereas a parabola deduced from the same number of points as the preceding ones, but bridging over the breaks, shows an error nearly four times greater than it ought to be, and an attempt to express even one-fourth of the whole of Jones's results as a single curve without any breaks leads to a parabola with an error 10,000 times greater than the experimental error. The author points out that even the most perfect agreement between the freezing point and conductivity results cannot disprove the existence of breaks, or of the

hydrates indicated by them, unless it is first proved that the conductivities are represented by a regular curve. This is far from being the case, and, moreover, the agreement between the two sets of results (even when Jones's values are accepted) is by no means perfect; it is only approximately so as far as a depression of 0·1°. S. U. P.

Freezing Point of very Dilute Solutions. By H. C. Jones (*Zeit. physikal. Chem.*, **11**, 529—551).—In continuation of his former experiments, the author has carefully determined the freezing point of dilute solutions of potassium sulphate, barium chloride, magnesium sulphate, cadmium chloride, cadmium bromide, cadmium iodide, cadmium nitrate, and zinc chloride. The following table shows for potassium sulphate the character of the accordance between the dissociation ratios calculated from the electrical conductivity (Kohlrausch) and from the freezing point:—

	Strength of solution (in equivalents).	Ratio from conductivity.	Ratio from freezing point.
K_2SO_4.....	0·002 normal	92·2 per cent.	94·1 per cent.
„	0·006 „	88·3 „	90·8 „
„	0·01 „	85·8 „	88·2 „
„	0·03 „	78·7 „	82·0 „
„	0·05 „	74·9 „	79·1 „
„	0·1 „	70·1 „	72·0 „

These results indicate that the dissociation ratio of salts may be more correctly ascertained from the electrolytic conductivity (Arrhenius) than from the solubility relations, as Noyes suggests.

J. W.

Dependence of the Solubility of a Solid on its Melting Point. By I. Schröder (*Zeit. physikal. Chem.*, **11**, 449—465).—For solids which dissolve in liquids without any change in the specific heats occurring, the author has deduced the two following relationships thermodynamically from the theory of osmotic pressure:—

$$\text{I. } \text{Log}_e S = \frac{\rho}{2} \cdot \frac{T_0 - T}{T_0 T}.$$

$$\text{II. } \frac{Q}{T} = \frac{\rho}{T_0} = \text{const.}$$

where S is the ratio of the dissolved molecules to the total number in the solution, ρ the molecular latent heat of fusion of the solid, T_0 its fusion point in the absolute scale, T the temperature at which the solution is saturated, and Q the molecular heat of solution of the solid in its almost saturated solution. Experiments on the solubility of paradibromobenzene in carbon bisulphide, benzene, bromobenzene, and ether, of naphthalene in benzene, chlorobenzene, and carbon tetrachloride, and of metadinitrobenzene in benzene, bromobenzene, and chloroform, gave results in fair accordance with these equations. The alcohols as solvents do not behave as those above mentioned, but are closely similar among themselves. The relationships may be expressed in words as follows: the solubility of different solids in

different liquids is the same when the temperatures are equally removed from the melting points of the solids. J. W.

Participation of a Solvent in Chemical Reactions. By W. NERNST (*Zeit. physikal. Chem.*, **11**, 345—351).—Considerable doubt still exists regarding the question of the nature of the action of a solvent on the soluble substance and in how far this may be considered a chemical action. The author attempts to gain some fresh light in this direction by considering the question from the point of view of the laws of mass action.

If we consider the action between the solvent and soluble substance to be of the kind $A + nB = AB_n$, and if c, c_1, and c_2 are the concentrations, then, in accordance with the Guldberg-Waage law, $Kc_2 = cc_1^n$. If the solvent B is present in large excess, so that its concentration can only change slightly with an alteration in the conditions of equilibrium, c_1^n may be regarded as constant, that is, the active mass of a solvent at constant temperature is practically constant. If we are dealing with two liquids, and suppose that π is the vapour pressure of the solvent, p that of the dissolved substance, and p_1 that of the solution, then $\pi p = K'p'$. But also $c = kp$ and $c_2 = k'p'$, so that $c_1^n = \pi \frac{K}{K'} \cdot \frac{k'}{k} = \pi \times$ const. From this it follows that the active mass of a solvent is proportional to its vapour pressure at constant temperature. H. C.

Permeability of Precipitated Membranes. By J. H. MEERBURG (*Zeit. physikal. Chem.*, **11**, 446—448).—The author has repeated some of Tammann's experiments on the permeability of certain precipitated membranes to dyes, choosing those examples which in Tammann's hands gave results contradictory to the "molecular sieve theory" (Abstr., 1892, 1383). The conditions of experiment were so far altered that the dyes were only added to the liquid on one side of the membrane after the membrane itself was completely formed. The results were occasionally irregular, but on the whole were in harmony with the "molecular sieve theory." J. W.

Cyclical Equilibria. By M. WILDERMANN (*Zeit. physikal. Chem.*, **11**, 407—425).—The main object of the present paper was to prove the deduction made by Ostwald from a study of the properties of the factors of chemical energy, that two substances or groups of substances which are each in equilibrium with a third are in equilibrium with one another. A heterogeneous system consisting of two liquids, bromine and water, which are but little soluble the one in the other, was selected, and free acids or salts soluble in the water, but not in the bromine, were afterwards introduced. The bromine dissolves in very different amounts in the different solutions, but the concentration of the vapour above the solutions always remains the same, and equal to that which it shows when water alone is taken. The chemical potential of the common constituent, the bromine, remains the same in all three parts of the different systems, and this may be regarded as proving the deduction above given. H. C.

Laboratory Burner. By N. Teclu (*J. pr. Chem.* [2], **47**, 535—536).—A description of an improvement in the new burner previously described (Abstr., 1892, 768), designed for the simultaneous regulation of the flow of gas and air. A. G. B.

Light Petroleum Burner. By G. Barthel (*Ber.*, **26**, 1179—1180).—The author describes a light petroleum burner consisting of a circular reservoir with two tubes at opposite sides; one is situated at the upper end, and is connected with a small hand bellows, by means of which the petroleum is forced through the second tube, which is at the lower end of the reservoir, and is bent at a right angle; the petroleum is vaporised in the tube, the vapour mixes with air, and is burnt in an ordinary Bunsen's burner. The reservoir is stated not to become unduly heated, and there is no danger of explosion. For a flame 10 cm. high, 40 grams of petroleum per hour are required; for one 20 cm. high, 135 grams. Iron wire, 0·3 mm. in diameter, readily burns with scintillation, and platinum wire, 0·1 mm diameter, quickly fuses. J. B. T.

Clay Filters. By W. Pukall (*Ber.*, **26**, 1159—1172).—A description of clay filters made by the Royal Porcelain Manufactory, Berlin. They are made of unglazed, hard-baked clay, so hard that steel will not scratch them, endure a pressure of several atmospheres without breaking, and are attacked, only, and then but to a very slight extent, by hot concentrated sulphuric acid, or caustic soda. They are made in the shape of a flask with flattened bottom, of capacity 50, 135, and 1000 c.c. in the respective sizes, and as cylinders 19 cm. long, of 50 c.c. capacity. These filter at the rate of, roughly, 4900, 8600, 29,600, and 5950 c.c. of pure water per hour respectively, with a difference of pressure of 700—720 mm; the rate is not much less when a turbid mixture is filtered instead of pure water. The filtration is very perfect; from water containing barium sulphate precipitated in the cold, or stannous sulphide, perfectly clear filtrates were obtained, and the complete washing of the precipitate was effected in from three-fifths to two-fifths of the time required with a folded filter. From milk and starch-solution perfectly clear filtrates were also obtained, but these became somewhat turbid on standing. The filter is usually immersed in the liquid to be filtered, and connected, several at once if required, with a large exhaustion-vessel, into which the clear filtrate runs; this vessel is exhausted by means of a water-pump, and then left to itself, a great saving of the water used by the pump is thus effected, as compared with the ordinary method of filter-pump filtration. The filters may be cleaned for further use by rubbing with sand, or, if this is not successful, by dipping in strong acids. If they have been used for filtering oil, for which they are also adapted, they may be cleaned by ignition in a muffle. C. F. B.

Hygroscopic Properties of Textile Fabrics. By T. Schloesing, Jun. (*Compt. rend.*, **116**, 808—812).—The author considers that in determinations of the hygroscopic properties of various compounds

sufficient attention has not been given to the influence of temperature and the coefficient of saturation of the atmosphere. In the case of cotton, wool, merino, and silk, however, the influence of temperature, although distinct, is comparatively small, and this seems to be true also of some other materials. Curves are given showing the relation between the temperatures and the quantity of water absorbed by the textile fabrics specified, when they are allowed to remain for a long time in contact with air having a known coefficient of saturation.

C. H. B.

Inorganic Chemistry.

Hydrogen Peroxide Solutions. By H. P. TALBOT and H. R. MOODY (*J. Anal. Chem.*, **6**, 650—661).—Commercial solutions of hydrogen peroxide were found to contain hydrochloric, sulphuric, phosphoric, and hydrofluosilicic acid, besides sugar, glycerol, barium, calcium, aluminium, and magnesium; in no case was a sample obtained sufficiently pure for direct use in analysis. To purify a commercial solution, it was mixed with 10 per cent. alcohol, and barium hydroxide in powder added to distinctly alkaline reaction, filtered, and the filtrate treated with a slight excess of sulphuric acid; the filtrate, after this treatment, contained 0·003 per cent. of silica, instead of 0·028 originally present. The alcohol was then removed by distillation under diminished pressure. Solutions of hydrogen peroxide may be concentrated by evaporation under diminished pressure; the loss of hydrogen peroxide under a pressure of 30 mm. only amounts to 5 per cent. when the quantity which has distilled over is also taken into account. In this manner solutions of such a concentration were obtained that when unit volumes were mixed with permanganate solution, 588 vols. of oxygen were evolved; whilst the distillates similarly treated evolved 19 vols. of oxygen. When hydrofluosilicic acid is present, it decomposes, and the silicon fluoride evolved reacts with the distillate, forming silicic and hydrofluosilicic acid. The statement that pure hydrogen peroxide solution has an acid reaction is incorrect.

For many purposes, a sufficient purification is effected by neutralising with potash, and allowing the precipitate of silica, potassium silicofluoride, &c., to settle; the supernatant liquid is then decanted through a ribbed filter. About 0·5 per cent. of sulphuric acid should be at once added to the filtered liquid to prevent decomposition.

A. R. L.

Preparation of Perchloric acid. By R. CASPARI (*Zeit. angw. Chem.*, 1893, 68—74).—See this vol., ii, 390.

Decomposition of Gaseous Hydrogen Iodide by Heat. By M. BODENSTEIN and V. MEYER (*Ber.*, **26**, 1146—1159).—Although the course of chemical reactions which take place in solutions has in

many cases been studied with great exactitude, the difficulties in the way of applying accurate measurement to changes taking place in gases are so great, that, up to the present, the only instance in which this has been successfully accomplished is that of the combination of hydrogen with chlorine, in the classical investigation of Bunsen and Roscoe, 36 years ago. To obtain, if possible, some further data with regard to the course of chemical change in gases, the authors have been led to study a reaction which, unlike the one above quoted, is of a reversible character, and in which, therefore, the establishment of a condition of equilibrium will be in no way influenced by such disturbing circumstances as are found to arise in other cases. The reaction selected was the decomposition of hydrogen iodide.

That this reaction is of a reversible nature is, of course, well known, but the authors were surprised to find with what ease combination between hydrogen and iodine takes place, on merely heating the two together, and in the absence of platinum or any other condensing agent. If a sealed tube, filled with hydrogen and containing a little iodine, is heated in sulphur vapour, formation of hydrogen iodide in considerable quantity takes place. The gas is also far more stable than has hitherto been supposed, as a sample of the pure gas was heated for a whole day in the vapour of boiling aniline without being in the least decomposed. Decomposition, at any rate of the pure gas, cannot therefore be said to commence at 180°, as is usually stated. The pure gas is, however, sensitive to the action of light. In bulbs which were exposed for 10 days to the direct action of sunlight, 58 per cent. of the gas was found to have suffered decomposition, and in bulbs freely exposed to sunlight throughout the whole of the summer, 99 per cent. of the gas was decomposed. The decomposition, although slow, is practically complete.

Hydrogen iodide, prepared from phosphorus iodide, cannot, with the utmost care, be completely purified from traces of phosphorus compounds. The gas used in these investigations was therefore prepared by the direct union of hydrogen with iodine in the presence of platinised asbestos. It was passed into water until this was completely saturated, and by gently heating this solution the gas was again obtained. It was then freed from moisture by means of phosphoric anhydride, and from iodine by means of red phosphorus. The gas was passed into glass bulbs provided with lateral capillary tubes, similar to those used by Krause and Meyer, in their investigation on the combustion of gaseous mixtures (Abstr., 1891, 1153). The bulbs had been previously completely freed from air by passing hydrogen through them for 20 hours, with occasional heating to dull redness. When filled with pure hydrogen iodide, the bulbs were sealed, and then submitted to the desired temperature by placing them in the vapour of some liquid of known boiling point. After being allowed to cool, they were opened below the surface of a solution of potassium hydroxide of sp. gr. 1·28, which had been previously boiled to free it from air; in this, hydrogen is practically insoluble. The volume of the gas (hydrogen) remaining unabsorbed showed to what extent the hydrogen iodide had suffered decomposition.

As eventually the direct formation of hydrogen iodide from its

elements under the conditions of the decomposition was also studied, it became necessary to introduce equivalent quantities of hydrogen and iodine into sealed tubes. This, at first sight, difficult operation was effected by taking glass tubes of about 30 c.c. capacity, and introducing into each the necessary quantity of iodine contained in a melting point tube. They were then filled with pure hydrogen, rarefied to $\frac{1}{2}$ atm., and sealed. These tubes were then submitted to a process similar to that above described.

Experiments were first made in the vapour of boiling sulphur (448°), retene (394°), and mercury (350°). As means from several experiments in each case, the following numbers were obtained:—

Temperature of boiling		Relative amount of HI decomposed, determined	
		By decomposition.	By direct union.
Sulphur.....	448°	0·2150	0·2104
Retene.....	394	0·1957	—
Mercury	350	0·1731	0·1738

Decomposition experiments were then made in diphenylamine vapour (310°), and gave as the relative amount of hydrogen iodide decomposed, 0·1669, in place of the expected number of 0·1550, calculated from the above determinations. The difference between the observed and calculated result in this case may be explained on thermodynamical grounds. The heat of formation of hydrogen iodide is at ordinary temperatures negative, but from the fact that the decomposition at high temperatures, 350—448°, increases with rising temperature, it follows from Van't Hoff's principle, that the heat of formation at these temperatures is positive. There must, therefore, be a temperature at which the heat of formation is zero, and at which also the decomposition is at a minimum. The point obviously lies between 310° and 350°, and according to a preliminary calculation from the above results is at 324°.

Since the above determinations show that regular conditions of equilibrium were in each case attained, and preliminary experiments rendered it probable that these were only gradually established, attempts were also made to study the decomposition as a time reaction. These proved to be perfectly successful, as it was found that two bulbs heated for the same length of time at the same temperature always gave the same result. The results were calculated by means of the formulæ:—

For the decomposition .. $\frac{dx}{d\theta} = C(1-x)^2 - C'\left(\frac{x}{2}\right)^2$.

For the combination .... $\frac{dx}{d\theta} = C'\left(\frac{1-x}{2}\right)^2 - Cx^2$.

These by integration gave equations from which the constants C and C′ could be calculated. The constancy in the values actually obtained for each of the above temperatures of experiment shows

that in the case of the decomposition of hydrogen iodide by heat the change is one which takes place in a perfectly regular manner.

H. C.

Azoimide from Hydrazine Hydrate and Nitrous acid. By T. CURTIUS (*Ber.*, **26**, 1263).—A dilute solution of azoimide may be conveniently prepared, as a lecture experiment, by passing the nitrous fumes from the action of nitric acid on arsenious anhydride into a cooled, dilute, aqueous solution of hydrazine hydrate until a permanent evolution of gas begins; or, better, by condensing the nitrous fumes on lumps of ice, and adding the blue liquid to the hydrazine hydrate until the evolution of gas begins. C. F. B.

New Synthesis of Azoimide. By T. CURTIUS (*Ber.*, **26**, 1263—1271).—See this vol., i, 463.

Hyponitrous acid. By C. PAAL (*Ber.*, **26**, 1026—1028; compare W. Wislicenus, this vol., ii, 318).—By the action of silver nitrite on hydroxylamine hydrochloride in aqueous (2 per cent.) solution at 0°, no evolution of gas occurs, and the liquid appears to contain hydroxylamine nitrite; after separation from the silver chloride, the clear solution is treated with silver nitrate and dilute ammonia until no further precipitate is formed; the insoluble portion is washed with water and dissolved in dilute nitric acid; on the addition of ammonia, an additive compound of silver nitrite and silver hyponitrite, $Ag_2N_2O_2,2AgNO_2$, is precipitated; it is deposited from solution in dilute ammonia in small, yellow, granular crystals which readily blacken in the dark.

By the action of nitrous acid on benzylhydroxylamine, benzyl alcohol is formed. J. B. T.

Constitution of Bleaching Powder. By J. MIJERS (*Zeit. anorg. Chem.*, **3**, 186—192).—A reply to the criticisms of Lunge (this vol., ii, 277) on the author's previous paper on this subject (this vol., ii, 209). A. G. B.

Formula of Bleaching Powder. By G. LUNGE (*Zeit. anorg. Chem.*, **3**, 351—352).—The author prefers to write $CaOCl_2,H_2O$, instead of $Ca(OH)_2Cl_2$, as the formula of bleaching powder (compare this vol., ii, 209). J. W.

Silicon. By H. N. WARREN (*Chem. News*, **67**, 136—137).—Aluminium, in pieces the size of a walnut, is introduced into a clay crucible containing a fused mixture of 4 parts of potassium silicofluoride, 1 part of potassium chloride, and 2 parts of potassium carbonate, and when the violent reaction has subsided, the mass is heated to whiteness for five minutes. When cool, the crucible is smashed; the button, carefully detached from adhering slag, is placed in a plumbago crucible with 12 parts by weight of aluminium and 2 of tin, and covered with a layer of sodium silicate; the mixture is submitted for two hours to the strongest heat obtainable. When cold, the piece of aluminium is broken, when the new modifica-

tion of silicon is found in large, lustrous, infusible, oblique octahedrons, insoluble in all acids except hydrofluoric. D. A. L.

Distribution of Calcium and Magnesium in Nature. By N. Lubavin (*J. Russ. Chem. Soc.*, **24**, 389—423).—The author discusses the comparative distribution of calcium and magnesium in the animal, vegetable, and mineral kingdoms, using the analytical data that have appeared in the *Jahresbericht* from 1857 to 1886. The solid crust of the earth contains more calcium than magnesium. Meteorites, on the other hand, contain more magnesium than calcium. Magnesium is contained in greater quantity in sea-water, most mineral springs, and in some lakes of Central Asia and Western Siberia; whilst in river water calcium prevails. In general, plants contain more calcium than magnesium, exceptions being found in cereals, some parts of the potato and beet, and in certain maritime plants. Animals also contain calcium in preponderating quantity.

The author has made several series of experiments on the solubility of calcium and magnesium carbonates in water, and in salt solutions, as well as on the double decomposition of the chloride of one metal and the carbonate of the other. The following table contains the solubilities at 26°, expressed in parts of metallic oxide in 100 parts of solution.

	In water.	In 2·525 per cent. solution of NaCl.
Precipitated $MgCO_3,3H_2O$ ..	0·0812	0·1250
Magnesite.....	0·0027	0·0048
Precipitated $CaCO_3$.....	0·0005	0·0037
Calcspar.....	0·0027	0·0053

Calcium carbonate, whether natural or precipitated, is not decomposed appreciably at ordinary temperatures by a solution of magnesium chloride, but magnesium carbonate is completely converted into magnesium chloride by a solution of calcium chloride, the length of time required for the conversion depending on the strength of the calcium chloride solution (compare Bothamley, Trans., 1893, 696).

J. W.

Double Fluorides. By H. v. Helmholt (*Zeit. anorg. Chem.*, **3**, 115—152).—The author has prepared double fluorides of ammonium and other metals by dissolving the hydroxide of the metal in ammonium fluoride and evaporating to crystallisation.

Most of the salts which he describes have been prepared before (compare Wagner, Abstr., 1886, 670); the following must now be added to the list:—The *beryllium* salt, $BeF_2,2NH_4F$, crystallises in small, colourless needles and prisms; the *cadmium* salt, CdF_2,NH_4F, is a white, crystalline precipitate; the *copper* salt, $CuF_2,2NH_4F,2H_2O$, forms blue crystals; the *antimony* salt, $SbF_3,2NH_4F$, crystallises in laminæ; the *bismuth* salt, BiF_3,NH_4F, forms transparent crystals. Of these, the copper, bismuth, and cadmium salts are insoluble in water.

The salts CuF_2,KF; CuF_2,RbF; and $CuF_2,NH_4F,2\frac{1}{2}H_2O$ were also prepared. A. G. B.

Dehydration of Cupric Hydroxide and its Basic Salts. By B. KOSMANN (*Zeit. anorg. Chem.*, **3**, 371—376).—The author endeavours to deduce the results obtained by Spring and Lucion (this vol., ii, 210) from thermochemical principles. J. W.

Nitrocopper. By P. SABATIER and J. B. SENDERENS (*Compt. rend.*, **116**, 756—758).—Nitrocopper is obtained by passing nitric peroxide at 25—30° over finely divided copper, obtained by the reduction of cupric oxide by means either of hydrogen or of carbonic oxide. Whether prepared with pure nitric peroxide, or with the peroxide diluted with nitrogen, it has the composition Cu_2NO_2. A small quantity of copper oxide is formed, the proportion increasing with the temperature at which the reaction takes place. Although stable in dry air, the nitrocopper, as previously stated, decomposes into copper and nitric peroxide above 90°, and is violently decomposed by water, with evolution of pure nitric oxide and formation of a solution of copper nitrite and nitrate. Hydrogen has no action in the cold, but if the temperature is rapidly raised to about 180°, ammonium nitrite and free ammonia are formed. Carbonic oxide has no action in the cold, but, on heating, nitric peroxide is given off, and reduced copper is left. Sulphurous anhydride has no special action, but on heating combines with the nitric peroxide that is evolved, and forms the well-known crystalline compound, a residue of partially oxidised copper containing some copper sulphate being left. Chlorine acts in the same way as on reduced copper, copper chlorides being formed, whilst the nitric peroxide is given off. Gaseous ammonia attacks the nitrocopper immediately in the cold, with formation of water vapour and white fumes of ammonium nitrite and nitrate, the mass then suddenly becoming incandescent with formation of large quantities of ammonium salts, whilst a residue containing copper and ammonio-copper oxides, but no copper nitride, is left. Hydrogen sulphide reacts with nitrocopper at the ordinary temperature, with formation of water and sulphur, and, finally, of bright blue cuprous sulphide.

Nitrocopper, in many reactions, behaves as if the copper and the nitric peroxide were intimately associated together, but each retained its own properties. It can therefore be used in many reactions in place of nitric peroxide. C. H. B.

Solubility of Mercuric Iodide in Diiodomethane. By J. W. RETGERS (*Zeit. anorg. Chem.*, **3**, 252—253).—Diiodomethane (100 parts by weight) dissolves 2·5 parts of mercuric iodide at 15°, 16·6 parts at 100°, and 58 parts at 180°. On slowly cooling the saturated solution, it deposits large, rhombic plates of the yellow modification, whilst by further cooling, especially in the presence of some of the ready formed substance, quadratic crystals of the red modification are obtained. A. R. L.

Action of Charcoal on Solutions of the Salts of the Rare Earths. By K. HOFMANN and G. KRÜSS (*Zeit. anorg. Chem.*, **3**, 89—91).—The neutralised hydrochloric acid solution of the rare earths

was heated on the water-bath with purified animal charcoal, in the expectation that the feebler bases would be precipitated on the surface of the charcoal. This was subsequently incinerated, and the residual oxide was purified by conversion into oxalate. The equivalent of the metal contained in this oxide was R''' = 155·94, that of the original having been 138·7.

Animal charcoal cannot be completely freed from phosphate, which vitiates the results. A sugar charcoal was therefore prepared. This, when submitted to the treatment described above, separated an earth which had the equivalent R''' = 134·4, that in the original earth having been 116·8. In another experiment, an yttria of R''' = 93·03 yielded, by a single treatment with charcoal, an earth giving R''' = 96. Such a result could not be achieved by a single precipitation with aniline. The amount precipitated is, however, very small; for instance, 8 grams of charcoal only separated 0·05 gram from 2 grams of earth. A. G. B.

Behaviour of the Gadolinite Earths with Potassium Chromate. By G. Krüss and A. Loose (*Zeit. anorg. Chem.*, **3**, 92—107).—The earth used in this investigation was prepared from gadolinite by a preliminary fractionation with ammonia (Abstr., 1891, 1424), followed by a precipitation of the nitrates of the middle fraction with potassium sulphate, and the further fractionation of the earths left in solution by ignition of their nitrates. The fraction submitted to treatment with potassium chromate had an equivalent of R''' = 102. A solution of the nitrate was mixed with potash until there was a slight precipitate, which was filtered off. Potassium chromate was added and the mixture warmed as long as the precipitate increased; the solution became red from the production of potassium dichromate. The precipitated chromate was dissolved in hydrochloric acid, reduced by alcohol, nearly neutralised by ammonia, and precipitated as oxalate. The filtrate from the chromate was again treated as described above; three such fractions were prepared. The first, contrary to expectation, gave a brown oxide, showing the presence of much didymium, the strongest of these bases; it had the equivalent R''' = 115·6; the second and third fraction gave lighter oxides and had the equivalents R''' = 111 and 104·3 respectively. Spectroscopic examination of the three fractions showed that the first was rich in didymium and erbium, which are respectively the strongest and weakest of these bases, whilst yttria appeared in the following fractions. It thus seemed probable that didymium was thrown down as chromate, and the erbium as basic chromate or free base, accounting for the production of potassium dichromate.

Further experiments showed that an approximate separation of didymium could be effected by precipitation with potassium chromate in a cooled solution, leaving the erbium to be precipitated on heating, together with more didymium, as basic chromates.

A preparation of didymium oxide, obtained by repeated precipitation with potassium chromate in the cold until the erbium lines disappeared from the spectrum, gave an equivalent R''' = 145·3, a result probably too high, but explicable in part by the fact that it

contained excess of oxygen, indicated by its brown colour. A heating in hydrogen showed that 0·5 per cent. oxygen had been absorbed in excess. The precipitate was proved to be a didymium chromate, and not a double potassium salt. A. G. B.

Action of Aniline and Aniline Hydrochloride on the Gadolinite Earths. By G. Krüss (*Zeit. anorg. Chem.*, **3**, 108—114).—The fractionation of these earths by aniline has been already dealt with (Abstr., 1891, 1425). If the bases can be fractionally displaced from their chlorides by aniline, it follows that the hydroxides must be fractionally soluble in aniline hydrochloride. The best method of applying this principle is to acidify the solution of the chlorides of the earths with hydrochloric acid, to add a quantity of aniline about equivalent to the earths in solution, and then ammonia equivalent to the quantity of earth which it is desired to precipitate; after warming for $1\frac{1}{2}$ hours at 80°, the precipitate is filtered off through a dry filter. If it be required to separate the feeble bases from the stronger, only a little ammonia is added, so that the precipitate may contain only the feeblest bases; if, on the other hand, the strongest bases are required, much ammonia is added, so as to leave these only in solution. The author designates the former process "aniline precipitation," and the latter "aniline solution." The method will be further developed. A. G. B.

Erbia. By G. Krüss (*Zeit. anorg. Chem.*, **3**, 353—369).—If ytterbium earths containing erbium are submitted to fractionation by decomposition of the nitrates by heat, or by the action of aniline or aniline hydrochloride, and if those fractions are considered as erbium earths which have an equivalent $Er''' = 166$—168 and show the absorption lines $\lambda = 654{\cdot}7$ and $\lambda_1 = 523{\cdot}1$, then an apparently homogeneous oxide is obtained, with the properties ascribed by Cleve to erbia. The same result is reached if fractional decomposition of the nitrates by heat alone is pursued far enough. When, however, apparently all the ytterbium, holmium, terbium, and yttrium have been removed by the above methods, and an erbium with a constant equivalent has been obtained, it is possible, by fractionation with aniline hydrochloride, to decompose the earth further into substances with different equivalents. Erbia is therefore not a homogeneous earth, but consists of several substances, further researches on which are promised by the author. J. W.

Behaviour of Aluminium towards Mercuric Salts. By J. Klaudy (*Chem. Centr.*, i, 1893, 201; from *Rep. Pharm.*, **3**, 89).—When aluminium is brought into an aqueous solution of mercuric chloride, aluminium amalgam is first formed, and subsequently it is decomposed by the water, the aluminium being converted into chloride. When aluminium is added to a concentrated alcoholic solution of mercuric chloride, a very energetic reaction ensues; mercury is first deposited on the aluminium, which latter slowly dissolves. When the mixture is warmed, the reaction becomes violent enough to cause the alcohol to boil, and when the reaction is complete, a small quantity of gas, probably hydrogen, is evolved. Ethylic chloride was not detected.

Towards the end of the reaction only is the alcohol decomposed, whilst the excess of aluminium dissolves as basic chloride. The amalgam produced at the first stage contained 1 part of mercury and 36·1 parts of aluminium. Other mercuric salts behave in the same manner as the chloride, and the amalgam is formed when chloroform or aldehyde is used as solvent. The amalgam has a great affinity for oxygen; it quickly becomes heated to 80° on exposure to the air, decomposes water, reduces potassium dichromate, permanganate, ferricyanide, indigo, nitrobenzene (in alkaline solution), and precipitates electropositive metals from their solutions. It dissolves readily in acids and alkalis, does not decompose absolute alcohol, decomposes dilute alcohol only to a slight extent, and is indifferent towards hydrocarbons.

A. R. L.

Volatility of Manganese at High Temperatures. By R. Lorenz and F. Heusler (*Zeit. anorg. Chem.*, **3**, 225—229).—The authors confirm the observations of Guntz concerning the non-existence of a manganese carbonyl at temperatures comparable with those at which ferrocarbonyl and nickel carbonyl are formed (Abstr., 1892, 568). When manganese carbide, Mn_3C, was heated to whiteness in a current of carbonic oxide, the metal was melted and the walls of the tube were covered with finely-divided manganese. But this was not due to the formation of a manganese carbonyl, for the same result was obtained when hydrogen or nitrogen was substituted for carbonic oxide. No absorption of the nitrogen by the metal was observed. The authors conclude that manganese is volatile at a temperature a little above its melting point (compare Jordan, Abstr., 1878, 772).

A. G. B.

Iron Chlorobromide. By C. Lenormand (*Compt. rend.*, **116**, 820—823).—Bromine acts very slowly on anhydrous ferrous chloride at the ordinary temperature, combination being incomplete even after a month. In sealed tubes at about 100°, the result varies with the proportion of bromine employed. If the chloride and the bromine are mixed in the proportions $2FeCl_2 : Br_2$, combination takes place, but no crystals are formed; if, however, the bromine is in excess, *ferric chlorobromide*, $Fe_2Cl_4Br_2$, separates in volatile crystals which are insoluble in excess of bromine. The crystals are lustrous, and very dark coloured, green by reflected light, and completely opaque even in thin sections. They seem to be hexagonal tables. The compound is very deliquescent, and very soluble in water; it also dissolves readily in alcohol or ether, and, by means of the latter, can be separated from ferrous chloride. Chloroform, benzene, and toluene also dissolve it, but carbon bisulphide dissolves only a trace. It is easily decomposed by heating, but sublimes readily when heated in a tube containing a slight excess of bromine.

When bromine is added to ferrous chloride solution, combination takes place with considerable development of heat, and, after expulsion of the excess of bromine, the composition of the liquid agrees with the formula $Fe_2Cl_4Br_2$. The solution is very deep red when concentrated, and yellow when dilute. It has an acid reaction, and contains colloïdal ferric oxide.

C. H. B.

History of Complex Inorganic Acids. By C. FRIEDHEIM (*Zeit. anorg. Chem.*, **3**, 254—263).—The author replies to certain remarks made by Kehrmann (*Zeit. anorg. Chem.*, **3**, 76) on his previous paper (Abstr., 1893, ii, 282). Finkener must be regarded as the discoverer of this class of compounds. A. R. L.

Complex Inorganic Acids. By F. KEHRMANN (*Zeit. anorg. Chem.*, **3**, 377—379).—A rejoinder to Friedheim.

Preparation and Specific Gravity of Uranium Dioxide. By W. F. HILLEBRAND (*Zeit. anorg. Chem.*, **3**, 243—248).—Wöhler obtained uranium dioxide by evaporating a solution of uranium oxychloride, UO_2Cl_2, with an excess of sodium and ammonium chloride, and fusing the residue. Uhrlaub (1861) stated that the product was a nitrogenous compound of the formula $U_{10}N_4O_{18}$. The author finds that when air is completely excluded during the fusion, an almost qualitative yield of uranium dioxide is obtained, and that Uhrlaub's compound does not exist or, at any rate, is not obtainable under the conditions mentioned. The specific gravity of crystallised uranium dioxide (reduced to a vacuum and compared with water at 4°) is certainly not lower than 10·95, and is probably 11. A. R. L.

Further Example of the Isomorphism of Thorium and Uranium Dioxides. By W. F. HILLEBRAND (*Zeit. anorg. Chem.*, **3**, 249—251).—When an oxide of uranium is fused with borax for 24 hours, and the cold mass extracted with water and dilute acetic or hydrochloric acid, jet-black octahedra of uranium dioxide are obtained. The appearance of the crystals is unaltered when thorium dioxide is one of the constituents of the mixture, as the latter is isomorphous with uranium dioxide. A. R. L.

Solubility of Metallic Iodides, &c., in Methylenic Iodide. By J. W. RETGERS (*Zeit. anorg. Chem.*, **3**, 343—350).—100 parts of methylenic iodide dissolve 22·9 parts of stannic iodide at 10°, the sp. gr. of the solution at that temperature being 3·481. The solubility increases rapidly with rise of temperature, the stannic iodide separating on cooling as highly refractive octahedra, with or without cubic faces. Arsenious iodide also dissolves in methylenic iodide to the extent of 17·4 parts in 100 of solvent. The solution is dark red, and has the sp. gr. 3·449 at 12°, the temperature of experiment. 100 parts of methylenic iodide dissolve 11·3 parts of antimonious iodide at 12°, giving a solution of sp. gr. 3·453. Bismuth iodide is much less soluble, only 0·15 part dissolving in 100 of the solvent at 12°. The solubility is scarcely affected by a rise of temperature.

Lead iodide, cadmium iodide, ferrous iodide, thallous iodide, mercurous iodide, cuprous iodide, and silver iodide are only dissolved in traces, if at all, by methylenic iodide. The boiling solvent does not dissolve the double compound $2TlI,HgI_2$, but partially decomposes it into its constituents.

10 parts of powdered sulphur dissolved in 100 parts of methylenic iodide at 10°. Melted sulphur mixes freely in all proportions with

methylenic iodide. 100 parts of the same solvent dissolve 1·3 parts of selenium, and 0·1 part of tellurium at 12°. Iodine is very soluble in methylenic iodide, and so likewise is yellow phosphorus, red phosphorus being quite insoluble. Neither arsenic nor antimony could be appreciably dissolved. J. W.

Specific Gravity of Titanium. By K. B. Hofmann (*Ber.*, **26**, 1025—1026).—The titanium employed was obtained as a fine powder by the action of sodium vapour on potassium titanium fluoride in an atmosphere of hydrogen. Two series of determinations made with 1·977 grams and 1·5944 grams of the metal, and calculated, according to Kohlrausch's formula, gave the sp. gr. = 3·4973 and 3·5888 respectively, of which the author believes the latter to be the more correct value. The atomic volume = 13·4. J. B. T.

Formation of Thiovanadates. By G. Krüss (*Zeit. anorg. Chem.*, **3**, 264—266; compare Abstr., 1890, 1381; 1891, 989).—By fusing together vanadic oxide, soda, and sulphur until the excess of the latter is driven off, the anhydrous salt Na_3VS_3O (*loc. cit.*) is obtained. A similar result was obtained by Norblad (*Upsala Univers. Arsskrift*, 1874). Potassium and ammonium salts cannot be obtained by the dry method as they undergo decomposition. A. R. L.

Constitution of Inorganic Compounds. By A. Werner (*Zeit. anorg. Chem.*, **3**, 267—330).—A theoretical paper devoted to the discussion of the so-called ammonio-metallic compounds. The formula of "platinosodiamine chloride" may be written $Pt(NH_3{\cdot}NH_3Cl)_2$ or $Pt(NH_2Cl{\cdot}NH_4)_2$. Jörgensen's observation that tertiary amines, as well as pyridine, form compounds analagous to these, favours the first formula, because although it is conceivable that two residues of ammonia may combine thus: $\equiv NH_2{\cdot}NH_4$, this cannot be the case with a tertiary amine in which the whole of the hydrogen is replaced by alkyl groups. A. R. L.

Composition of the Precipitate obtained with Hydrogen Sulphide in Solutions of Potassium Iridiochloride. By U. Antony (*Gazzetta* **23**, i, 184—190).—Berzelius and Fehling (Fehling's *Handwörterbuch*, **3**, 812) state that iridium bisulphide is obtained by the action of hydrogen sulphide on solutions of iridic chloride or potassium iridiochloride; contradictory observations are, however, recorded by Claus (Gmelin-Kraut, *Handbuch*, **3**, 1311). The author has, therefore, again investigated the action of hydrogen sulphide on solutions of potassium iridiochloride. Pure iridium, prepared by the author's method (Abstr., 1892, 1285), was mixed with potassium chloride, and heated at 300° in a stream of chlorine; the iridiochloride was then extracted with boiling water and crystallised. On passing hydrogen sulphide through a 2 per cent. aqueous solution of the salt at 90—100°, a brown precipitate separated, and the solution gradually lost its dark colour, but, even after prolonged passage of the gas, it still remained reddish-yellow; the precipitate was collected, washed with hydrogen sulphide solution, avoiding contact with the

air, and dried at 90° in a stream of carbonic anhydride. The powder thus obtained underwent no alteration in the air and contained no free sulphur; it was analysed by roasting it to metal in a stream of air, and gave results which in the author's opinion show it to be a mixture of iridium bisulphide and sesquisulphide approximating in composition to $2IrS_2,Ir_2S_3$. This view is also supported by the persistent colour of the solution from which the sulphide was precipitated, the sesquisulphide being slightly soluble in water. The chlorine, which would be liberated if iridium sesquisulphide were formed, should oxidise the hydrogen sulphide to sulphuric acid, and accordingly sulphuric acid was found in the solution. If the treatment with hydrogen sulphide takes place at 20—30°, a smaller proportion of sesquisulphide is formed, the precipitate approximating in composition to $6IrS_2,Ir_2S_3$; at 0° a still larger proportion of the bisulphide is present in the precipitate.

The observations of the older workers on this subject are hence erroneous. W. J. P.

Lithium Iridiochloride and Iridium Bisulphide. By U. Antony (*Gazzetta*, **23**, i, 190—194).—*Lithium iridiochloride* may be prepared by passing dry chlorine over a mixture of iridium with carefully dehydrated lithium chloride at 300°; the salt is then extracted with water and crystallised. It is thus obtained in minute, garnet-red needles, which are somewhat deliquescent; on drying at 90—100° in a current of air, it forms a dark red powder.

The author has shown (see preceding abstract) that the precipitate formed by hydrogen sulphide in iridium solutions is a mixture of iridium bisulphide and sesquisulphide; it is hence impossible to obtain the bisulphide by the wet method. It may, however, be prepared by passing hydrogen sulphide over lithium iridiochloride at 4—7°; no action occurs below 0°, and at above 10° the salt is very rapidly attacked with formation of free sulphur. On repeatedly extracting the mass with absolute alcohol and drying the residue at 90—100° in a current of carbonic anhydride, *iridium bisulphide*, IrS_2, is obtained as a brown powder, which is not affected by exposure to moist air. It is partially decomposed by water with separation of sulphur, and when heated at 300° in the air it gives metallic iridium; it is not attacked by hydrochloric acid or ordinary nitric acid, but is readily decomposed by fuming nitric or nitrohydrochloric acid. On heating at a low red heat in a current of carbonic anhydride, it loses sulphur, as already stated by Berzelius, yielding iridious sulphide. W. J. P.

Osmium. By H. Moraht and C. Wischin (*Zeit. anorg. Chem.*, **3**, 153—179).—The black osmium oxide, originally obtained by Eichler by the action of nitric acid on potassium osmate, and supposed by him to be $K_2O,3OsO_2$, was afterwards obtained by Fremy, and again by Claus and Jacoby, by exposing a solution of potassium osmate to sunlight; the latter chemists assigned to it the formula $OsO_2,2H_2O$.

The authors have reinvestigated this substance, dried over phosphoric anhydride in a vacuum until constant in weight, and find that

it is osmic acid, H_2OsO_4. It was analysed in several ways with concordant results; the methods are described in the paper.

Osmic acid is sooty-black, and when dry does not possess any of the coppery lustre alleged by Claus and Jacoby to be characteristic of $OsO_2,2H_2O$. In moist air, it has a strong odour of perosmic anhydride, but is stable under water which contains alcohol. It dissolves in nitric acid to perosmic anhydride, and in boiling hydrochloric acid to an olive-green solution which smells of chlorine. It is not attacked by sulphuric acid.

When hydrogen sulphide is passed over osmic acid, a violent reaction occurs, much heat is evolved, and osmium oxysulphide, $Os_2S_2O_2,H_2O$, is formed. This is a brown powder, which is decomposed and dissolved by nitric, hydrochloric, and sulphuric acids (compare E. v. Meyer, Abstr., 1878, 14). Considering the high temperature which accompanies the formation of this compound, the authors are of the opinion that the hydrogen must be present in the form of OH or SH, and quote some evidence in support of the formula $O(OsO{\cdot}SH)_2$. By further heating in hydrogen sulphide, it is converted into OsS_2.

Osmic acid was heated with strong hydrochloric acid in a reflux apparatus for 48 hours, a little alcohol being added to hinder the formation of perosmic anhydride; chlorine was evolved, and a slight, black residue left undissolved; after filtering and evaporating in a vacuum, large, well-formed, six-sided pyramids of the chloride $Os_2Cl_7,7H_2O$ were obtained. In moist air this salt is dark, olive-green, but when absolutely dry it is the colour of minium; it dissolves in alcohol and water with a dark green colour and crystallises again unchanged. It would appear, however, that this chloride is a mixture of $OsCl_4$ and $OsCl_3$; for when its alcoholic solution is mixed with a solution of potassium chloride, potassium osmium chloride, K_2OsCl_6, separates in the form of red octahedra, and if the filtrate from this be evaporated in a vacuum, a crystalline residue of $OsCl_3,3H_2O$ is left.

Osmium is not attacked by bromine vapour. When osmic acid is treated with hydrobromic acid, in the manner described above for hydrochloric acid, small, dark brown, prismatic crystals having the composition $Os_2Br_9,6H_2O$ are isolated. This compound appears to be made up of $OsBr_3$ and $OsBr_6$, and is being further investigated. Indications of the existence of an oxybromide were obtained.

There is no reaction between osmium and iodine vapour, nor between osmic acid and iodine vapour. The iodide obtained by heating osmic acid with hydriodic acid was difficult to analyse, but appeared to be OsI_4. It forms violet-black crystals which appear to be rhombohedra, and have a metallic lustre; it dissolves to a red-brown solution in alcohol and in water, and when the solution in aqueous alcohol is heated, a black powder is deposited which has a coppery lustre when dry, and appears to be an oxyiodide.

The existence of an osmium oxyfluoride was proved.

A. G. B.

Mineralogical Chemistry.

Sundite, a new Mineral from Oruro, in Bolivia. By C. Brögger (*Zeit. Kryst. Min.*, **21**, 193—199).—In a collection of Bolivian minerals presented to the Christiania University by L. Sundt, there is a series of specimens of a new silver ore. The mineral, which resembles tetrahedrite in appearance, crystallises in the rhombic system. It is very brittle, and has a hardness of 3 to 4, and a sp. gr. of 5·5. Analysis yielded the following results:—

Cu.	Ag.	Fe.	Sb.	S.	Total.
1·49	11·81	6·58	45·03	35·89	100·80

The formula is probably $(Ag_2Cu_2Fe)S,Sb_2S_3$.

Sulphantimonates of similar composition have not hitherto been met with in nature. B. H. B.

Melanostibian, a new Swedish Mineral. By L. J. Igelström (*Zeit. Kryst. Min.*, **21**, 246—248).—At the celebrated Sjö manganese mine, in the Government of Orebro, where numerous rare minerals have been discovered, a new antimony mineral has been found occurring in veins 1 to 2 cm. in width in dolomite. This has been named *melanostibian* by the author, from μέλας (black) and the Latin *stibium* (antimony). The mineral is black, its powder being cherry-red. Its hardness is 4. Analysis gave the following results:—

Sb_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
37·50	27·30	29·62	1·97	1·03	1·06	98·48

It formula is $6(MnFe)O,Sb_2O_3$. B. H. B.

Melanophlogite. By E. Mallard and G. Friedel (*Bull. soc. fran. min.*, **13**, 180 and 356).—In an exhaustive description of this mineral from the Solfatara Giona at Racalmuto, an analysis is given of absolutely pure melanophlogite, the results being as follows:—

SiO_2.	SO_3.	Fe_2O_3.	
93·18	6·19	0·29	B. H. B.

Titaniferous Iron Ore from the Breitfirst. By R. Wedel (*Zeit. Kryst. Min.*, **21**, 259).—In a description of the dolerite district of the Breitfirst, a range of hills extending from the Rhone to the Spessart, the author gives analyses of plagioclase, augite, and titaniferous iron ore from the doleritic plagioclase-basalt of the district. Analysis of the titaniferous iron ore from the unweathered (1) and the weathered (2) rock gave the following results:—

	TiO_2.	Fe_2O_3.	FeO.	MgO.	Total.	Sp. gr.
I.	45·03	11·18	42·59	1·89	100 69	4·68
II.	47·08	13·06	39·97	0·84	100·95	4·69

B. H. B.

Physiological Chemistry.

Influence of dividing the Daily Nutriment on the Metabolism of the Dog. By C. Adrian (*Zeit. physiol. Chem.*, **17**, 616—633).—Full details are given of the metabolic exchanges in a dog fed, first, on a given amount of flesh, and secondly, on the same amount divided into four portions in the course of the day. In the latter case, there was an increase in body weight, in nitrogen output, and in output of urea. An increased absorption of proteïd takes place if the four meals are given instead of one. Under such circumstances, the amount of loss by the fæces is diminished, and also less proteïd is broken up by pancreatic and bacterial action into simple products which are of little use to the organism.

The application of this to the dieting of human individuals is obvious. W. D. H.

Sugar in Muscle. By A. Panormoff (*Zeit. physiol. Chem.*, **17**, 596—606).—The amount of sugar in muscle is very small in warm-blooded animals, from 0·01 to 0·03 per cent. It does not come from the blood in the muscles, as muscles freed from blood yield about the same quantity. The sugar is dextrose, identified by the phenylglucosazone which was made from it. There is no evidence of maltose in muscles, as Pavy (*Lancet*, 1881, ii, 5 and 43) has stated. The glycogen in muscles disappears after death, but there is no corresponding rise in sugar; probably it forms lactic acid.

W. D. H.

Goat's Milk. By Schaffer (*Chem. Centr.*, 1893, i, 620—621; from *Schweiz. Woch. Pharm.*, **31**, 58—60).—See this vol., ii, 396.

The Acids of Ox Bile. By Lassar-Cohn (*Zeit. physiol. Chem.*, **17**, 607—615; compare Abstr., 1892, 1114, 1503).—Further investigations have not led to the identification of any further acids in ox bile. The methods described, employed on large quantities of ox bile, have led to the following quantitative results. The acids given below are those organic acids which are precipitated by hydrochloric acid after boiling with sodium hydroxide. There is a total percentage of 5·195, made up as follows:—

Cholic acid	4·790
Choleïc acid	0·085
Stearic acid, Palmitic acid, Oleïc acid	0·146
Myristic acid	0·004
Resinous acids	0·120
	5·145
Loss	0·050

W. D. H.

Uric acid in the Organism. By C. WULFF (*Zeit. physiol. Chem.*, **17**, 634—643).—The experiments of Horbaczewski (Abstr., 1892, 646) are not conclusive, as the uric acid he obtained must have been contaminated with xanthine. A method is described for the quantitative separation of these two substances, which depends on the fact that dilute hot nitric acid breaks up uric acid into higher oxidation products, whilst xanthine is not affected. W. D. H.

Action of Nitrites on Muscular Tissue. By J. T. CASH and W. R. DUNSTAN (*Proc. Roy. Soc.*, **52**, 91—93).—Experiments on skeletal muscles of the frog were conducted in an air-tight chamber, so constructed as to permit of connection being made between the muscle and recording apparatus, and also so that the vapour of a known quantity of nitrite could be introduced. The nitrites produce shortening; their order of activity in relation to the extent of this shortening is (1) isobutylic, (2) tertiary amylic, (3) secondary butylic, (4) secondary propylic, (5) propylic, (6) tertiary butylic, (7) butylic, (8) α-amylic, (9) β-amylic, (10) ethylic, (11) methylic. The order representing the speed with which shortening occurs is (1) methylic, (2) ethylic, (3) secondary propylic, (4) tertiary amylic, (5) primary propylic, (6) tertiary butylic, (7) secondary butylic, (8) α-amylic, (9) β-amylic, (10) primary butylic, (11) isobutylic.

In minute doses, insufficient to cause passive contraction, nitrites lessen the irritability of muscle.

This physiological action is not solely, and in some cases not even mainly, dependent on the amount of nitroxyl (NO_2) they contain. In all phases of physiological activity, the secondary and tertiary are more powerful than the corresponding primary compounds; this is due to the great facility with which they are decomposed into the alcohol and nitrous acid. In accelerating the pulse, the power of the nitrites is directly as their molecular weight, and inversely as the amount of nitroxyl they contain. The same relationship holds, although less uniformly, in their power of reducing blood pressure and inducing muscular contraction. This appears to be due to the increased chemical instability which the substituted methyl groups confer on the higher members of the series. The reverse order holds for the most part in relation to the duration of subnormal pressure, and the rapidity of the onset of muscular contraction. The simpler nitrites probably attach themselves to certain constituents of blood and muscle, and thus act more quickly than the higher compounds, whilst their greater stability causes their effect to last longer.

A large proportion of organic nitrite is changed into nitrate in its passage through the organism, and is excreted in the urine as an alkali nitrate. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Are Nitrates Indispensable for the Growth of Plants? By O. Pitsch (*Landw. Versuchs-Stat.*, **42**, 1—95; compare Abstr., 1888, 84).—The paper gives the results of experiments made from 1886 to 1891. The plants were grown in poor sandy soil, containing about 0·11 per cent. of nitrogen, and supplied in each case with the necessary mineral constituents, without nitrogen, with nitrogen as nitrate, and with nitrogen as ammonia. In each set of experiments, the ammonia was applied as sulphate, and in some cases, also, as phosphate. The plants employed were barley, wheat, oats, beetroot, and beans. The soils were sterilised as already described (*loc. cit.*). In 1888, an alteration was made in the apparatus, so that water could be applied at the surface of the soil. The following table gives the results of all the experiments (except those with ammonium phosphate, which do not differ materially from those in which the sulphate was employed), and shows the amount of nitrogen applied and the amount of dry produce.

The growth was normal in each case, but was generally much less where there was no nitrate than when nitrate was given. The pots which had no application of nitrogen gave generally as much growth as those supplied with ammonia. Different plants seem to behave

	Ammonium sulphate.		Sodium nitrate.		Soil.	
					Sterilised and extracted.	Not sterilised and extracted.
Barley grown in (1) 1886–87, (2) 1888, *and* (3) 1890.						
1 Total N applied....	0·595		0·773	0·862	—	(0·78)
1 Dry produce	39·8		63·8	63·8	—	64·9
2 Total N applied....	0·515	0·347	0·703	0·463	—	—
2 Dry produce	17·9	24·5	37·2	34·0	14·0	20·0
3 Total N applied....	0·8143	0·8523	0·8284	0·8347	—	—
3 Dry produce	48·2	(12·5)*	100·9	(34·9)*	57·6 (10·2)*	—
Wheat grown in 1886–87.						
Total N applied.....	0·557		0·56	0·56	—	(0·557)
Dry produce.....	58·1		70·0	61·9	—	70·6

* These plants were cut at an early period of growth.

	Ammonium sulphate.		Sodium nitrate.		Soil.	
					Sterilised and extracted.	Not sterilised and extracted.
Oats grown in (1) 1889, (2) 1890, *and* (3) 1891.						
1 Total N applied....	0·876	0·435	0·8827	0·4315	—	—
1 Dry produce	23·7	20·7	74·1	66·7	24·7	65·2
2 Total N applied....	0·652	0·649	0·651	0·649	—	—
2 Dry produce	13·4	15·8	82·0	75·9	20·1 14·5	—
3 Total N applied....	0·810	0·409	0·810	0·409	—	—
3 Dry produce	17·8	28·5	77·1	55·1	36·7* 13·0	—
Beetroot grown in (1) 1887, (2) 1888, (3) 1889, *and* (4) 1891.						
1 Total N applied....	0·439		0·434		—	—
1 Fresh produce	159·4		169·9		—	—
2 Total N applied....	0·788	1·712	0·822	1·643	—	—
2 Dry produce	79·7	92·4	83·9	142·3	—	137·1
3 Total N applied....	2·200	1·169	2·356	1·136	—	—
3 Dry produce	48·3	53·8	181·6	119·6	33·6	—
4 Total N applied....	2·241	2·241	2·241		—	—
4 Dry produce	55·9	74·8	117·7		66·8	—
Beans grown in 1887.						
N per kilo. of soil	0·0118		0·0116		—	—
Dry produce.....	27·2		41·2		—	—

* Top dressing contains 0·135 gram of nitrogen.

differently towards ammonia; in the case of oats, the difference between the nitrate and ammonia plants was always very considerable. The plants grew in sterilised soil as well as in soil not sterilised, when both soils contained nitrogen in the same form. Beans, when grown in soils which had been heated at 100°, behaved like barley; they were able to develop when supplied with ammonia, but were much stronger when grown in presence of nitrate. With the single exception of winter wheat, all the plants were much more benefited by nitrate than by ammonia, the difference being shown not only by the production of a heavier crop but more especially in the earlier stages of growth, when the presence of nitrate seems to be

most necessary. The presence of nitrate in the soil seems to enable the plant to take up more nitrogen in other forms (ammonia?) than when the soil was left unmanured or was supplied with ammonia. In every case (except wheat) the nitrate plant utilised much more of the nitrogen of the soil present in other forms than nitrate (ammonia?) than the ammonia plants did. The more favourable action of nitrate was evident in every stage of development of the plants, and the plants so manured were always the first to ripen.

The young plants seemed particularly sensitive towards ammonia, the corn plants losing early the points of the first leaves, whilst the leaves of the beetroot plants showed brown spots and died earlier than those which received nitrate. This difference was especially noticeable when the young plants were exposed to the sun.

There is evidence that, in the course of the experiments, nitrification did not take place in the sterilised pots, and that nitrifying bacteria do not occur in the air. N. H. M.

Analytical Chemistry.

Electrometric Analysis. By R. Behrend (*Zeit. physikal. Chem.*, **11**, 466—491).—The author proposes to use a sensitive electrometer as an indicator in volumetric analysis as follows: If, for example, a two-fluid cell is constructed, having for electrodes mercury, and for liquids solutions of mercurous nitrate and potassium chloride, then a large electromotive force will be observed between the poles. If, now, a solution of mercurous nitrate is added from a burette to the solution of potassium chloride, the electromotive force sinks at first slowly, but with slightly increasing velocity as more mercurous nitrate enters the liquid, until at the point when all the halogen present has been precipitated by the mercurous salt, it suddenly falls to a value not far removed from zero. The point at which the sudden fall takes place indicates when equivalent quantities of the reagents are present. Thus, in the above case, the amount of halogen in the potassium chloride solution may be estimated by titration with mercurous nitrate. The author has made corresponding experiments with silver salts and silver electrodes, and finds that, by using ammoniacal solutions, he can not only estimate the total halogens in the mixture but the amount of iodine separately. J. W.

Use of Sodium Peroxide in Analysis. By W. Hempel (*Zeit. anorg. Chem.*, **3**, 193—194).—The author points out that this compound can now be obtained free from sulphur, nearly free from chlorine, and containing some 60—70 per cent. of sodium peroxide, the rest being sodium oxide. For the usual method of detecting chromium and manganese it is admirable, and is much to be recommended for decomposing tungsten minerals and titanic iron ores. It serves excellently for attacking sulphides whose sulphur is to be determined, only for this

purpose it must be diluted with half its weight of soda, otherwise the reaction is explosively violent; 1 part of the mineral to 2 parts of soda and 4 parts of sodium peroxide is recommended. The heating is conducted in a silver crucible, and the reaction is over in a few minutes. The mass is dissolved in water, any ferric oxide filtered off, and the sulphuric acid determined as usual. Results are quoted to show the concord between the results obtained by such a method and those obtained by solution in aqua regia. A. G. B.

Estimation of Chlorides, Hypochlorites, and Chlorates in presence of each other. By M. ROSENBAUM (*Zeit. angw. Chem.*, 1893, 80).—*Estimation of Calcium Chloride in Bleaching Powder.*—An aliquot part of the original solution is boiled to destroy the hypochlorite, and the solution is afterwards titrated with silver nitrate using potassium chromate as indicator. (Allowance should, of course, be made for the chloride formed by the decomposition of the hypochlorite. —ABSTRACTOR.)

Estimation of Calcium Chlorate.—An aliquot part of the solution is boiled for some time, then cooled and mixed with a definite quantity of ferrous ammonium sulphate and an excess of sulphuric acid. The mixture is now boiled, again cooled, and the excess of iron is then titrated back with permanganate. The amount of chlorate is easily found by calculation. (Allowance must, of course, be made for the chlorate produced from the hypochlorite.)

Estimation of Calcium Hypochlorite.—This estimation, on which, of course, the accuracy of the other determinations depends, is done by Pennot's process by means of arsenious acid and iodine solution. Free chlorine is also occasionally present in samples of bleaching powder, but the author states that the amount is so small that its estimation may be safely neglected. L. DE K.

Estimation of Oxygen in Iron. By P. GLADKY (*Chem. Centr.*, 1893, i, 440—441; from *Russ. Berg. J.*, **2**, 81—83).—In the estimation of oxygen in iron by heating the metal in a current of hydrogen and weighing the water produced, errors may accrue from the absorption of oxygen during the filing or boring to obtain the sample. A sample of iron containing 0·65 per cent. of carbon gave on analysis 0·082 per cent. of oxygen, which latter amount is improbable, taking into account the high percentage of carbon. Experiments to obtain samples by covering the iron with mercury during the boring failed because the mercury contained occluded air. The ferrous oxide which is contained in the occluded slag is reduced when heated in a current of hydrogen; when the iron itself contains no ferrous oxide; this error, however, is of little importance, since slag is itself an objectionable constituent. The results cannot be controlled by weighing the sample before and after heating in a current of hydrogen, and ascertaining whether the loss in weight of the iron, multiplied by $\frac{8}{9}$, corresponds with the gain of the absorption apparatus, because the carbon and sulphur in the sample are also converted into volatile hydrogen compounds.

A. R. L.

Estimation of Sulphur in Iron. By W. SCHINDLER (*Zeit. angw. Chem.*, 1893, 11—13).—Meineke has attempted to prove that commercial iron, when treated with hydrochloric acid, does not yield all its sulphur as hydrogen sulphide, and that a not inconsiderable amount is left in the insoluble residue, and must be estimated. Hattensaur has, however, demonstrated that Meineke's ideas are incorrect, and that there is no reason to distrust the time-honoured hydrogen sulphide process of estimating the sulphur.

The author, having made a few experiments, states that Meineke has made the mistake of using an acid of insufficient strength (sp. gr. 1·1) and that this causes, indeed, an incomplete expulsion of the sulphur. By using a strong acid of 1·19 sp. gr., every trace of sulphur was obtained as hydrogen sulphide.

The author passes the gases evolved on dissolving the sample through a solution of bromine in hydrochloric acid, and afterwards estimates the sulphuric acid thus produced. L. DE K.

Estimation of Nitrogen in Nitrates and in Nitric acid. By J. STOKLASA (*Zeit. angw. Chem.*, 1893, 161—163).—The author, having tried the recent processes for the estimation of nitrogen in nitrates, states that the methods proposed by Schlösing-Grandeau, Lunge, Stutzer, and Devarda all yield accurate results. If, however, the assay must be done in a very short time, it is best to use Lunge's nitrometer.

Another fairly rapid process is the one proposed by Devarda (compare this vol., ii, 343). Devarda's reducing alloy is readily prepared by melting in a Hessian crucible 50 parts of copper, and adding first 45 parts of aluminium and then 5 parts of zinc. L. DE K.

Estimation of Phosphoric acid in Wines. By MORGENSTERN and A. PAVLINOFF (*J. Russ. Chem. Soc.*, **24**, 341—346).—The authors estimate the phosphoric acid in wines directly (without evaporating and calcining) as follows:—200 c.c. of the wine is placed in a conical flask and boiled until most of the alcohol has been removed. To the hot liquid, 20 c.c. of nitric acid, sp. gr. 1·38, is added in portions, the boiling being continued until the oxides of nitrogen have been largely got rid of. On cooling, the liquid is neutralised with ammonia, 50 c.c. of ammonium citrate solution, prepared according to Märker's direction, is added, and then 25 c.c. of magnesia mixture is dropped in with continual shaking. Ammonium magnesium phosphate separates almost at once as a finely crystalline, easily washed precipitate, which gives a perfectly colourless pyrophosphate on ignition.

The results obtained in this way agree with the determinations made by the molybdate method in the ash within about 1 milligram of P_2O_5 in 100 c.c. of wine. J. W.

Analysis of Bone Meal, Fish Guano, and similar Phosphatic and Nitrogenous Manures. By W. HESS (*Zeit. angw. Chem.*, 1893, 74—79; 148).—The author points out how difficult it is to get a thoroughly trustworthy sample. In order to get the exact relation between the phosphoric acid and the nitrogen, the estimation of these

constituents should be effected in such a way that only one weighing-out is required. 5 grams of a well mixed sample is heated in a Kjeldahl flask with 35 c.c. of strong sulphuric acid and 0·5—1 gram of mercuric oxide, and then boiled for about 1½—2 hours until decomposition is complete. After diluting with water, the contents are made up to 500 c.c. For the estimation of the nitrogen, 200 c.c. (= 2 gram substance) is distilled with aqueous soda and the ammonia estimated as usual.

For the estimation of the phosphoric acid, 50 c.c. of the filtered solution is mixed with 50 c.c. of Märker's solution of ammonium citrate and 20 c.c. of magnesium mixture. After a few hours, the precipitate is filtered off and treated as usual. L. DE K.

Preparation of Perchloric acid and Estimation of Potassium in presence of Non-volatile Acids by means of the same. By R. CASPARI (*Zeit. angw. Chem.*, 1893, 68—74).—The ordinary methods for the preparation of perchloric acid being somewhat costly and even dangerous, the author proposes the following process :—A Hessian crucible, 15 cm. in height, is filled with pure potassium chlorate, and is heated in a brick oven until the mass, liquid at first, has become a thickish paste. The fusion generally takes about 1½ hours. The fused mass is reduced to powder and boiled with 1½ times its weight of water. By this means the potassium chloride is dissolved, and, after cooling, the insoluble mass is rinsed with cold water and dried.

The potassium perchlorate is now dissolved in 7 times its weight of hot water and precipitated with a slight excess of hydrofluosilicic acid. After gently boiling for an hour, with occasional addition of hot water, the solution is allowed to cool and poured off from the jelly-like potassium silicofluoride. The liquid is evaporated on the water-bath and then allowed to remain in a cold place for 24 hours, which causes the separation of any remaining potassium compound. Solution of barium chloride is now added until precipitation ceases, and the filtrate is again evaporated until whitish fumes make their appearance. It is then filtered from any traces of potassium or sodium perchlorate, the filtrate is freed from barium by the cautious addition of sulphuric acid, and after standing for a few days, the reagent is ready for use.

Estimation of Potassium in presence of Non-volatile Acids.—The author fully confirms the statement of Wense (this vol., ii, 46), that potassium perchlorate is practically insoluble in commercial absolute alcohol to which 0·2 per cent. of perchloric acid has been added. He also has proved the complete solubility of the perchlorates of iron, aluminium, and calcium, and even of lead, although the alcoholic solution of the latter soon decomposes. The author objects to the use of weighed paper filters, but uses a weighed asbestos filter.

The process seems applicable, not only in presence of volatile acids, such as nitric or hydrochloric, but also of non-volatile acids, such as phosphoric, boric, oxalic, or tartaric, provided they are soluble in alcohol. Sulphuric acid does, however, interfere, but may be removed by the cautious addition of barium chloride.

When estimating potassium in presence of phosphoric acid by

evaporating with perchloric acid, and extracting the residue with the acid alcohol, a little phosphoric acid is liable to remain insoluble, but it may be completely removed by a second treatment with the perchloric acid. L. DE K.

Analysis of Crude Salt and Brines and Calculation from the Analytical Data. By J. WIERNIK and S. WIERNIK (*Zeit. angw. Chem.*, 1893, 43—47; 148).—The real object of an analysis of crude salt, or its mother liquors, is to find out the exact amount of sodium chloride it contains, but in the present state of affairs it is rather too much left to the discretion of the analyst how the results are to be calculated. In fact the operator may, if he chooses, calculate a certain amount of chlorine which really exists as sodium chloride into the comparatively worthless magnesium salt. The author proposes to estimate the amount of magnesium chloride directly, and this may be done very accurately by extracting the sample with absolute alcohol, which readily dissolves the magnesium chloride, but leaves the sodium compound undissolved. The magnesium salt may be calculated either from the weight of the magnesium pyrophosphate obtained from it, or more conveniently from the amount of chlorine.

When dealing with brines, these should be first evaporated to dryness. L. DE K.

Quantitative Analysis by Electrolysis. By A. CLASSEN (*Zeit. anorg. Chem.*, **3**, 211—219).—The author criticises some of the methods proposed by Rüdorff (this vol., ii, 93), and objects to the statement that electrolytic methods heretofore published contradict each other, and are of little value. A. G. B.

Electrolytic Analysis. By F. RÜDORFF (*Zeit. anorg. Chem.*, **3**, 370).—A reply to Classen.

Estimation of Aluminium in Ferroaluminium. By H. v. JÜPTNER (*Chem. Centr.*, 1893, i, 665; from *Öst. Zeit. Berg.- u. Hüttenwesen*, **41**, 110—112).—The estimation of aluminium in samples of ferroaluminium containing a large percentage of this metal may be conducted as follows:—The sample is dissolved in sulphuric or hydrochloric acid, and the silica separated as usual; a portion of the solution is oxidised and ammonia added, and the precipitate containing aluminium and ferric oxides and phosphoric acid is weighed, the iron being estimated by titration in another portion, whilst in a third the phosphoric acid is estimated. The percentage of aluminium is thus arrived at by a simple calculation. A sample analysed by this method gave Al = 12·31 per cent. and by Neuhausen's method it gave Al = 12·64 per cent.

A. G. Neuhausen's Method.—5 grams of the sample is dissolved in dilute sulphuric acid, the solution evaporated to dryness, the residue taken up with a little sulphuric acid, and diluted to 300 c.c. 100 c.c. of the filtrate is reduced with iron wire, neutralised with sodium carbonate, and poured into mixed boiling solutions of potassium cyanide and potassium hydroxide: for 1 gram of substance, 20 per cent. potash (50 c.c.) and 20 per cent. potassium cyanide (40 c.c.) are

used. The precipitate is collected and washed well, or the liquid is diluted to 500 c.c., filtered, and to 300 c.c. of the filtrate (= 1 gram substance) ammonium nitrate together with $1\frac{1}{2}$ times its amount of potash added, heated for an hour, and the alumina collected and washed. It must be tested for potash and iron; the latter must be estimated by dissolving the precipitate in concentrated hydrochloric acid and titrating with stannous chloride and iodine solutions, or with potassium thiosulphate after digestion with potassium iodide. All the reagents must of course be tested for aluminium.

A. R. L.

Chemical Investigation of Steel. By L. Schneider (*Chem. Centr.*, 1893, i, 365—366; from *Öst. Zeit. Berg.- u. Hüttenwesen*, **41**, 15—17).—*Estimation of Phosphorus in Steel.*—2 grams of steel shavings are dissolved in nitric acid (sp. gr. 1·2; 30 c.c.) and a concentrated solution of potassium permanganate (2 c.c.) dropped into the boiling solution, the boiling being continued for a short time. The precipitated manganic oxide is dissolved by the addition of a few drops of ferrous sulphate solution, and the solution filtered from silica. To about 30 c.c. of the solution, double the volume of ammonium molybdate solution is added, and the mixture warmed on the water-bath at 80°. The flask is then fitted with a caoutchouc stopper, and the mixture shaken; after 10 minutes, the phosphomolybdate precipitate is collected, washed with ammonium nitrate solution, rinsed off the filter into a porcelain capsule with ammonia, evaporated, cautiously heated to expel the ammonium salts, and weighed: 0·012 gram of the precipitate is equivalent to 0·01 per cent. of phosphorus in the sample. The ammonium molybdate solution is prepared by dissolving molybdic anhydride (100 grams) in aqueous ammonia (300 c.c.), diluting with water (100 c.c.), pouring the solution into nitric acid (sp. gr. 1·2; 1250 c.c.), and stirring at a temperature of 85°.

Estimation of Phosphorus in Iron Ores, Slags, &c.—2 grams of the pulverised sample is moistened with concentrated hydrochloric acid (10 c.c.) and evaporated in a platinum capsule with the addition of concentrated sulphuric acid (2 c.c.) and hydrofluoric acid (10 c.c.) until white fumes of sulphuric anhydride appear. The residue is boiled with nitric acid (sp. gr. 1·2; 10 c.c.) and water (20 c.c.). The filtrate is mixed with the molybdate solution, and the remainder of the operation conducted as already described.

The percentage of phosphorus may be estimated volumetrically as follows:—The phosphomolybdate precipitate is washed with water containing ammonium sulphate, and dissolved in ammonia; the solution is then acidified with hydrochloric or sulphuric acid, reduced with zinc, and titrated with potassium permanganate at a temperature of 40—50°. According to F. A. Emmerton, the quantity of permanganate corresponding with 100 parts of iron is equivalent to 90·7 parts of molybdic anhydride, or to 1·62 parts of phosphorus; whilst according to v. d. Pfordten, the same quantity of permanganate is equivalent to 85·7 parts of molybdic anhydride and 1·53 parts of phosphorus. The results calculated on Emmerton's values agree with those obtained by gravimetric analysis.

A. R. L.

Gas-volumetric Estimation of Nickel. By SYSSOYEFF (*Chem. Centr.*, 1893, i, 230—232; from *Mon. Sci.* [4], **6**, 865—868).—A quantity of nickel salt corresponding with 0·25 gram Ni is dissolved in about 100 c.c. of water and treated with an excess of potassium cyanide, whereby a solution of potassium nickel cyanide, $K_2Ni(CN)_4$, is obtained. To this is added 1:2 sodium hydroxide solution (30—40 c.c. ?) and chlorine passed into the mixture, when the following reaction occurs, $2K_2Ni(CN)_4 + 3KClO + 6Cl_2 = 7KCl + 8(CN)Cl + Ni_2O_3$, and the nickelic oxide, which is all precipitated in a few minutes, is collected on an asbestos filter, and washed with warm, faintly alkaline water. The method consists in measuring the oxygen which results from the action of the oxide on hydrogen peroxide thus:—$Ni_2O_3 + H_2O_2 = 2NiO + H_2O + O_2$. It is carried out in a modified Lunge's gas-volumeter, which is described with the aid of a drawing. The separation of nickel and iron is effected by Moore's method (Abstr., 1888, 631). A. R. L.

Nickel Analysis. By S. H. EMMENS (*J. Anal. Chem.*, **6**, 643—650).—By the electrolytic precipitation of copper from acid solutions containing nickel, the latter metal is also thrown down when a strong current is employed. The author recommends the precipitation of the copper as sulphide, and, from the filtrate, after oxidation that of the iron, &c., as hydroxide; if much iron is present, the washed precipitate is boiled with a very small quantity of dilute sulphuric or hydrochloric acid, whereby the whole of the nickel together with a small quantity of iron is dissolved; the latter is then precipitated in the filtrate by ammonia and ammonium chloride. The iron precipitate may be boiled with dilute ferric sulphate solution instead of with dilute acid. A. R. L.

Potassium Ferrocyanide. Detection of Hydrocyanic acid in presence of Ferrocyanides. By W. AUTENREITH (*Arch. Pharm.*, **231**, 99—109).—Potassium ferrocyanide is by no means so stable in the presence of dilute acids as is generally supposed; carbonic anhydride at 72—74° liberates hydrocyanic acid from it, potassium ferrous ferrocyanide, $K_2Fe_2(CN)_6$, being precipitated; artificial digestive fluid, peptone, and caseïn each exercise, at blood heat (37—40°), a similar action. Potassium ferrocyanide is not a poison; hydrocyanic is doubtless liberated from it in the stomach, and continuously, but in quantity so small that it is absorbed by the system as fast as formed, and undergoes further chemical change, so that a lethal dose has no time to accumulate. The only certain way to detect hydrocyanic acid or simple cyanides in presence of potassium ferrocyanide is to distil with a considerable amount of sodium hydrogen carbonate, and examine the distillate for hydrocyanic acid. If the presence of mercuric cyanide is suspected, a few c.c. of sulphuretted hydrogen water must be added, in addition to the carbonate, which does not itself decompose mercuric cyanide. C. F. B.

Higher Alcohols and other Impurities in Ethyl Alcohol. By E. GOSSART (*Compt. rend.*, **116**, 797—800).—The author has de-

termined the limits of sensitiveness of the capillary method of analysis (Abstr., 1892, 236) for the various impurities commonly found in ordinary alcohol. An alcohol will only roll in drops on its own surface when its strength is not less than 20°, and an alcohol of 20° will roll only on alcohol of a little more than 19° and a little less than 21°; alcohol of 25° admits of somewhat wider limits; whilst from 40° to 90° an alcohol will roll upon another which does not differ from it by more than 5°. These results are independent of the impurities present in the alcohol.

The analytical method is based upon the fact that when n c.c. of an alcohol of N° is diluted with N c.c. of water, an alcohol of n° is obtained. If, therefore, the alcohol to be examined is stronger than 20°, 20 c.c. of it is gradually diluted with water, the volume added when it just begins and when it just ceases to roll on alcohol of 20° being carefully observed. The mean of the two volumes, N, gives the strength of the alcohol. When the alcohol is of a strength lower than 20°, 20 c.c. is mixed with 20 c.c. of alcohol of 39·2°, and water is added until the rolling begins and ceases, the volume required, P, in c.c., gives the strength in degrees.

For the detection of impurities, it is advisable to dilute the alcohol to 25°. In the case of amyl alcohol, a difference in composition of 0·5 per cent. prevents the rolling. The best standard is alcohol of 25°, containing 0·6 per cent. of amyl alcohol. Butyl alcohol behaves in a strictly analogous manner, and requires a similar standard liquid. In the case of propyl alcohol, the standard should contain 0·7 per cent. For acetone, the standard should contain 0·3 per cent., and alcohol of 25° containing less than 2 per cent. of acetone rolls on pure alcohol of 25°. For aldehyde, the sensitiveness is not sufficient to be of practical value, but the method may be usefully applied in the case of the impurities in tailings. C. H. B.

Estimation of Phenols in Crude Carbolic acid. By G. Schacherl (*Chem. Centr.*, 1893, i, 324—325; from *Zeit. allg. österr. Apoth. Vereins*, 1892, **35**).—Carbolic acid which is only slightly soluble in aqueous alkali (100 grams), or the purer kind, (50 grams), is shaken in a separating funnel with 9 per cent. aqueous sodium hydroxide (100 c.c.). The alkaline liquid is then run off, the oil once more extracted with 100 c.c., and, finally, two or three times with 50 c.c. of alkali. The combined alkaline extracts are mixed with an equal volume of water, and distilled until oily drops no longer pass over, indicating the absence of hydrocarbons; the residue is then acidified with hydrochloric acid and again distilled, using a large condenser, when the phenols pass over as a heavy oil. The distillation is stopped when the distillate measures 200 c.c., the oil is separated from the aqueous portion, and the latter returned to the distillation flask; the distillation is now again continued, and after a while interrupted, the oil being mixed with the first portion, and the aqueous layer returned to the distillation flask. The distillation is now repeated in this manner until the distillate no longer contains oily drops; the final aqueous distillate measures only 60—70 c.c., and is placed, together with the phenols, in a measuring cylinder. It is

shaken with an excess of common salt, allowed to separate into layers, and the volume of the upper layer, consisting of phenols, read off. The resinous substances remain in the distillation flask.

Carbolic acid of a still better grade (amount not stated) is introduced directly into the distillation flask, together with sodium hydroxide solution (300 c.c.) and treated as above described.

The mixture of phenols which has remained in contact with the sodium chloride solution contains 9 per cent. (by vol.) of water; since, however, phenols are soluble in concentrated brine, 5—6 per cent. too much cresol is found by direct reading. Red carbolic acid contains 11 per cent. of water, the technical product being, as a rule, saturated with water. By crude carbolic acid, the author means a product containing at least 50 per cent. of cresols. A. R. L.

Estimation of Uric acid. By F. G. Hopkins (*Proc. Roy. Soc.*, **52**, 93—99; also *Chem. News*, **66**, 106).—The urine is saturated with solid ammonium chloride (about 30 grams to 100 c.c.); the urates are precipitated as ammonium urate, which is collected, treated with hydrochloric acid, and the uric acid which separates out may then be estimated by any accustomed method.

This method is not only simpler and more rapid than others in use, but is as accurate as the standard Salkowski-Ludwig method.

W. D. H.

Recognition of the Radicle Benzoyl in Organic Compounds. By E. Léger (*Bull. Soc. Chim.* [3], 796—798).—Ferreira da Silva devised a method for the detection of cocaïne, in which some milligrams of the substance is evaporated on the water-bath with nitric acid (sp. gr. 1·4), and the residue added to concentrated alcoholic potash, when the odour of peppermint is developed. Subsequently Béhal found that the compound formed is ethylic benzoate. The author finds that the same odour is developed by similarly treating benzoylnaphthol, populin, aconitine, and other compounds containing the benzoyl radicle, a fact which renders the method useless as a specific test. A. R. L.

Detection of Cineole in Ethereal Oils. By E. Hirschsohn (*Chem. Centr.*, 1893, i, 503; from *Pharm. Zeit. Russ.*, **32**, 49—51).—While experimenting on the solubility of iodole (tetriodopyrroline) in ethereal oils, the author observed that cajeput, camphor, eucalyptus, and other oils dissolved iodole at first, but a crystalline compound subsequently separated out, which was readily soluble in ether and alcohol, but only sparingly so in chloroform. This reaction is due to the presence of cineole in the oils. As a test, it is carried out as follows:—3 to 15 drops of the oil is introduced into a test-tube, and shaken with 0·01—0·05 gram of iodole. If dissolution does not occur, more of the ethereal oil is added drop by drop, and when a clear solution is formed, it is allowed to remain for 24 hours. The supernatant liquid is then poured from the crystals, which are washed with light petroleum, and subsequently boiled with potash, when the odour of cineole will be developed. A list of ethereal oils which did not exhibit the reaction is subjoined. A. R. L.

Estimation of Fat in Milk. By Weiss (*Chem. Centr.*, 1893, i, 589—590; from *Pharm. Zeit.*, **38**, 87).—30 c.c. of milk is introduced into a flask of 300 c.c. capacity, and then mixed with 3 grams of officinal sodium hydroxide solution; light petroleum (60 grams) is added in three portions, and the mixture shaken after each addition until the liquid is quite homogeneous. If the last portion of petroleum does not mix readily, the liquid is placed aside for ¼ hour, after which mixing is easily brought about. The emulsion may be kept without separating for a day, but after adding 20 grams of alcohol and shaking the liquid frequently, separation is effected in six hours, and at the end of 24 hours three liquid layers have formed: the lowest is clear, and of a yellow colour, the middle one somewhat turbid, whilst the upper one, which is clear and colourless, contains the whole of the fat. An aliquot weight of the latter (petroleum solution) is then evaporated in a flat dish at 50°, and the residue dried at 100°.

Instead of weighing the fat solution, 25 c.c. of the milk is shaken with 3 c.c. of sodium hydroxide solution, and subsequently with 3 portions of light petroleum (25 c.c. each). 50 c.c. of the fat solution is then evaporated, and the fat weighed and calculated to 100 c.c. of milk. A. R. L.

Modification of the Reichert-Meissl Method. By H. Kreis (*Chem. Centr.*, 1893, i, 234—235; from *Schweiz. Wochenschr. Pharm.*, **30**, 481—483).—The principle of this method is the saponification of the glycerides of butter fat by means of concentrated sulphuric acid; hydrolysis is effected thus much quicker than by means of potash.

Five grams of the anhydrous fat is melted in an Erlenmeyer's flask closed with a loose fitting stopper, and, after being heated in a water-bath at a temperature of 30—32° for some minutes, concentrated sulphuric acid (10 c.c.) is added. The flask, placed horizontally, is rotated round its vertical axis until the contents are quite clear, when it is replaced in the water-bath. At the expiration of 10 minutes, water (150 c.c.) is added, and the mixture distilled as in the Reichert-Meissl method. A. R. L.

Goats' Milk and its Detection in Admixture with Cows' Milk. By Schaffer (*Chem. Centr.*, 1893, i, 620—621; from *Schweiz. Woch. Pharm.*, **31**, 58—60).—The author finds from numerous analyses that the composition of goats' milk lies between the following limits:—Water, 86·74—90·46 per cent.; fat, 2·14—4·72 per cent.; milk-sugar, 2·07—4·77 per cent.; proteïds, 2·3—4·38 per cent.; ash, 0·51—0·93 per cent. A sample of butter from goats' milk contained:—Water, 11·23 per cent.; fat, 87·38 per cent.; solids other than fat, 1·39 per cent.; the pure fat had a sp. gr. at 100° = 0·8668, and melted at 30°; its saponification value (Köttstorfer) was 226; its Reichert-Meissl value, 24; and its refraction (Amagat and Jean), 31·5°. These values are too close to those obtained with cows' milk to enable the two to be differentiated. The most pronounced difference between the fats, besides their distinctive odour and taste, is the want of colour of the ethereal extract of the fat from goats' milk. A. R. L.

Detection of Foreign Fats in Wool Fat. By W. Graff (*Chem. Centr.*, 1893, i, 504).—The author criticises Helbing and Passmore's method (this vol., ii, 351) adversely, and he states that it was employed in 1888 by Kremel. The saponification test can be conducted in a reflux apparatus, but the method can only be regarded as a qualitative test for glycerol. A. R. L.

Analysis of Bees-wax. By R. Benedikt (*Chem. Zeit.*, **16**, 1922).—The author defends his modification of Hübl's process against the criticism of Röttger (this vol., ii, 351), but admits that for the detection of less than 5 per cent. of paraffin or ceresin, the process recommended by Buisine should be used (compare Abstr., 1892, 1034). L. de K.

Some Toxicological Reactions. By J. Stern (*Zeit. angw. Chem.*, 1893, 136—138).—1. Reactions of Oils of Pimento and Cloves.—The author has found that the two oils give the same reactions with ethereal solution of bromine, alcoholic hydrochloric acid, sulphuric acid, Fröhde's reagent, ferric chloride mixed with sulphuric acid, nitric acid, picric acid, lime water, and alcoholic solution of ferric chloride. When in a fairly pure state, the oils may be distinguished by their odour, but when isolated from the contents of a stomach, the smell is generally too much obscured to be trustworthy.

2. Behaviour of Strychnine Nitrate with Hydrochloric acid.—The author points out that the reddish colour generated by heating strychnine nitrate with hydrochloric acid is also given by sugar, which renders the test practically worthless in toxicological investigations. L. de K.

The Estimation of Emetine in Ipecacuanha Root and in the Fluid Extract of the same. By C. C. Keller (*Chem. Centr.*, 1893, i, 235—236, 322—324; from *Schweiz. Wochenschr. Pharm.*, **30**, 501—505 and 509—514).—The author has investigated several of the methods which have been proposed for the estimation of alkaloïds in narcotic extracts, and he finally decides that Schweissinger and Sarnow's method (*Pharm. Centralh.*, 1890, **31**, 771) is by far the best.

For the estimation of emetine in fluid extract of ipecacuanha, the mode of precedure is as follows:—8 grams of the extract is diluted with an equal weight of water, chloroform (32 grams), and ether (48 grams) added, and the mixture well shaken; ammonia (4 grams) is now added and the shaking continued for 30 minutes. After the mixture has settled, 50 grams of the chloroform-ether layer is filtered into a tared flask, distilled, and the varnish-like residue washed twice with 5—10 c.c. of ether; the emetine is then dried in a water-bath and weighed. After this, it is dissolved in hot absolute alcohol (10 c.c.), water added until a permanent turbidity is produced, and the liquid titrated with N/10 hydrochloric acid in the presence of hematoxylin solution until the colour is pure yellow. The results are calculated on the formula $C_{30}H_{40}N_2O_5$ (Kunz, Abstr., 1887, 980), the equivalent value of which (254) was established by special experiments with pure emetine.

For the estimation of emetine in ipecacuanha root, the following method has been found to yield satisfactory results:—10 grams of the powdered root dried at 90—100° is shaken for some minutes in a dry glass vessel with a mixture of chloroform (40 grams) and ether (60 grams); on the addition of 10 grams of ammonia (officinal strength) and rotating the mixture, the suspended matter sinks to the bottom of the vessel, and the emetine is dissolved. The mixture is shaken for an hour, and, after this, another 5 grams of ammonia is added. 50 grams of the clear chloroform-ether solution is now distilled, the residue treated twice with 10 c.c. of ether, dried, and the emetine weighed. As, however, the root contains about 0·3 per cent. of fat, the presence of which vitiates the titration, this latter substance should be previously removed. To accomplish this, 10 grams of the dry, powdered root is placed in a small funnel which is plugged with a wad, and washed with 10—15 c.c. of ether until the filtrate is colourless. The residue is then washed into a tared glass with ether, and the latter, after being made up to 60 grams, is mixed with chloroform (40 grams), and the process conducted as above. The test analyses were satisfactory, and they show that the requirement of the Swiss Pharmacopœia, that ipecacuanha root should contain at least 2·5 per cent. of emetine, is not excessive. Choline, which Kunz and Arndt have found in ipecacuanha root, is neither extracted by ether (Dieterich) nor by a mixture of ether and chloroform.

The author promises to make known a simple method whereby an approximately quantitative yield of emetine may be obtained.

A. R. L.

A Sensitive Reaction for the Detection of Bile Pigments in Urine. By H. Rosin (*Chem. Centr.*, 1893, i, 368—369; from *Berlin. klin. Wochenschr.*, **30**, 106—107).—The Tiedemann-Gmelin test usually fails in those cases in which the presence of bile pigment is doubtful, and this is also the case when Fleischl's or Masset's modifications are employed. The author makes use of iodine for the detection of bilirubin in urine, the colouring matter being thereby oxidised to biliverdin, an observation due to Maréchal.

The process is carried out as follows:—An alcoholic solution of iodine is prepared by diluting 10 parts of tincture of iodine with 100 parts of alcohol. This reagent is then added to the urine, to be tested in such a manner that the two liquids do not mix; at the expiration of a minute, or even before, a grass-green ring will be formed at the surface of contact of the two liquids; it is permanent for an hour. In the absence of bile pigment, the urine is decolorised by the reagent, so that there is formed at the place of contact of the two liquids a bright yellow, or colourless, ring. A. R. L.

Precipitation of Proteïds from Blood preparatory to the Estimation of Sugar. By J. Seegen (*Chem. Centr.*, 1893, i, 369—370; from *Centr. Physiol.*, **6**, 604—607).—After numerous experiments, the author finally adopted the following method:—To 50 c.c. of the blood, 5 c.c. of acetic acid (sp. gr. 1·04) is added, together with 8—10 times the volume of water; the mixture is heated to incipient boiling, 9—10 c.c. of a 20 per cent. solution of sodium

carbonate gradually run in, and the liquid kept in ebullition for some minutes, after which it is filtered through a conical linen bag. The coagulum is repeatedly washed with water, the linen filter pressed, and the filtrate and washings concentrated to a known volume and finally filtered. It is now quite clear, and remains so on testing with acetic acid and potassium ferrocyanide; when acidified with hydrochloric acid and treated with potassiomercuric iodide, however, a more or less copious precipitate is produced. The solution is well adapted for titrating. A. R. L.

A Sensitive Reaction for the Detection of Albumin in Urine. By E. SPIEGLER (*Chem. Centr.*, 1893, i, 368; from *Centr. klin. Med.*, **14**, 49—52; compare Abstr., 1892, 928).—The reaction is obtained by a solution of tartaric acid and mercuric chloride containing glycerol; 1 part of albumin in 250,000 may be detected by the formation of a white ring at the point of contact of the urine and the reagent. The author no longer employs sugar in preparing the reagent, as the latter is found to keep better without it. Urine containing iodine cannot be tested by the reaction; bromine compounds do not, however, interfere with it.

Under the influence of slight indisposition, the urine of certain persons otherwise in sound health contains frequently small amounts of albumin, which cannot be detected by the ferrocyanide-acetic acid test. A. R. L.

Analysis of Rubber Goods. By R. HENRIQUES (*Chem. Zeit.*, **16**, 1595—1596; 1623—1624; 1644—1645).—The author first points out the great difficulty of obtaining a fair sample. Soft rubber goods must be cut into tiny pieces, well mixed, and a fairly large quantity taken for analysis; hard rubber may be divided by means of a rasp. The estimation of the amount of ash is not always quantitatively useful. If the sample contains, say, siliceous matter, or barytes, the results are fairly accurate; but if the mineral matter consists of lead carbonate, red lead, &c., the ash found will be too low and cannot, of course, serve as a measure for the amount of true rubber. Then again, even supposing the ash to represent the true amount of mineral matter, there is no certainty that the rubber does not, to a certain extent, consist of other organic matter, or so called rubber substitute. Another difficulty is the presence of sulphur which may afterwards wholly, or partially, be found as an apparent constituent of the ash.

The author recommends the following process for the estimation of the total sulphur. A deep porcelain basin is covered with a funnel with a short stem, and 20 c.c. of fuming nitric acid is put into it. 3 or 4 grams of the finely cut up sample is then by degrees introduced through the opening of the funnel. When the violent action is over, the dish is warmed on the water-bath, the solution is evaporated to a syrup and then treated with 4 grams of a mixture of 3 parts of potassium nitrate and 4 parts of sodium carbonate. After drying is complete, the mass is gently fused until all carbonaceous matter has disappeared. The mass is now treated

with hydrochloric acid, evaporated to dryness to render silica insoluble, and then taken up with dilute nitric acid. If, as usual, an insoluble residue remains, it consists of silica, barium sulphate, and lead sulphate, the latter of which may be dissolved out by means of ammonium acetate, and added to the main solution. The silica and barium sulphate are separated by the usual method, and should the main fluid contain sulphates there cannot be any further quantity of barium. The sulphuric acid is now estimated in an aliquot part of the acid filtrate by means of barium chloride. Another portion of the filtrate is used for the estimation of any metal supposed to be present.

To ascertain how much sulphur is present as vulcanising sulphur, as distinct from metallic sulphides or sulphates, the author uses the following process:—Commercial light petroleum is shaken with aqueous soda to remove sulphur compounds, dried, and distilled, the fraction coming over between 140—250° being collected. 5 grams of the sample, or 12 grams if it is rather low in ash, is placed in a weighed 250 c.c. flask, and 150 c.c. of the petroleum is added. After connecting the flask with a reflux condenser, it is heated in an oil-bath up to 140—150°, until the rubber is quite disintegrated and an insoluble deposit has formed at the bottom of the flask. A higher temperature should be avoided to prevent formation of hydrogen sulphide. After cooling, the solution is poured through a weighed filter, and the residue is washed a few times, finally with light petroleum of low boiling point. The flask and filter are now both dried at 110° and reweighed, and the amount of insoluble matter is thus obtained in which the sulphur may be estimated as directed. The difference between the two estimations represents the vulcanising sulphur.

As regards rubber surrogates, the author has come to the conclusion that alcoholic soda is the most convenient reagent. 3—5 grams of the finely cut up sample is digested with 10 times its weight of 8 per cent. alcoholic soda in a reflux apparatus. The solution is diluted with water and evaporated in a dish until the alcohol is expelled. The insoluble residue is now collected on a weighed filter, dried at 100°, and weighed. As it always contains mineral matter, besides a little soda which washing has failed to remove, the ash should be taken (ammonium nitrate being employed), and a sulphur estimation should then be made. As hard rubber is but imperfectly soluble in light petroleum, its inorganic constituents cannot be separated by this process, but rubber surrogates may be extracted by alcoholic soda. It is as yet impossible to ascertain what proportion of the vulcanising sulphur belongs to the rubber and what to the surrogate. L. DE K.

General and Physical Chemistry.

Determination of the Intensity of Rays. By N. Teclu (*J. pr. Chem.* [2], **47**, 568—583).—Crookes' radiometer has been adapted by the author for the purpose of determining radiant transparency (diaphanity). The radiometer is so arranged that its velocity of rotation is determinable, there being proportionality between the velocity of rotation and the intensity of the light falling on the radiometer. Tables are given showing the relative transparencies of different liquids. H. C.

Molecular Refraction of Compounds containing Nitrogen (Aldoximes and Ketoximes). By C. Trapesonzjanz (*Ber.*, **26**, 1428—1433).—The author has determined the molecular refractions of a number of aldoximes and ketoximes, with the view of obtaining evidence as to whether the nitrogen in these compounds is behaving as a triad element, or as suggested by Bischoff in the stereoisomeric formulæ

$$\begin{matrix} X \\ Y \end{matrix}\!\!>\!C\!-\!N\!<\!\!\begin{matrix} O \\ H \end{matrix}, \text{ and } \begin{matrix} X \\ Y \end{matrix}\!\!>\!C\!-\!N\!<\!\!\begin{matrix} H \\ O \end{matrix},$$

as a pentad. For sodium light and using the Lorenz formula, the molecular refraction of the group NOH was found to be in the aldoximes 6·575 and in the ketoximes 6·518, the mean value being 6·538. If for the atomic refraction of nitrogen the value, 2·870, given by Loewenherz be accepted and the atomic refractions O′ = 1·521 and H = 1·051, the calculated value for the group NOH is 5·442. The difference between this and the observed value may either be due to the increment for the double linkage between carbon and nitrogen, for which Brühl has given the value 0·92—1·11, or if instead of O′ we take O″ = 2·287, the calculated value then becomes 6·208, and no longer differs so considerably from that observed.

H. C.

Spectra of the Flames of some Metallic Compounds. By G. D. Liveing and J. Dewar (*Proc. Roy. Soc.*, **52**, 117—123).—Nickel carbonyl, when mixed with hydrogen and burnt in oxygen at a porcelain jet, exhibits a spectrum which consists of two parts, (1) the spectrum of the main body of the green flame, and (2) that of the base of the flame. The spectrum of the main body consists of a series of shaded bands, brightest in the green, but extending on the red side beyond the red lithium line, and on the violet side well into the blue. These bands have their sharp edges on the more refrangible side. Besides the bands, a few visible lines appear, only one of which, λ 5476, is a known line of nickel. In the ultra-violet part, however, a great number of nickel lines were photographed. In the spectrum of the base of the flame there are two principal groups of lines, one in the orange and red, the other in the citron and yellow. None of them appear to be nickel lines.

Zinc ethide, when burned with hydrogen so as to reduce the luminous spectrum, showed the following zinc lines, λ 4812, 4721, and 4681. There were no lines of zinc in the ultra-violet.

J. W.

Flame Spectra of some Metals. By D. Cochin (*Compt. rend.*, **116**, 1055—1057).—The author has photographed the ultra-violet portion of the flame spectra of the salts of certain metals, using a spectrograph with quartz prisms and quartz and Iceland spar lenses, the sensitive gelatinobromide film being curved so that all the rays were in focus. In all cases the water-bands at λ 309 were obtained, but in no case were there any lines or bands of higher refrangibility even with somewhat longer exposures. With a hydrogen flame, the spectra are somewhat more luminous, but the results are practically the same.

Lithium gives the line at λ 413. Sodium gives the double line λ 330·3 and 330·2 obtained by Kayser and Runge in the electric arc. Potassium gives the lines λ 404 and 344·4. Rubidium, in addition to the visible line λ 420, gives the two doublets, observed by Kayser and Runge, at λ 359·1—358·7 and 335·1—334·8, especially if the hydrogen flame is used, Cæsium gives the lines λ 388, λ 361·5, and λ 347·75 in addition to the visible blue lines λ 459·7—450. The first two correspond with two pairs mentioned by Kayser and Runge, whilst the third also seems to correspond with a line seen by them.

Calcium, strontium, and barium give the visible lines in each case, but no ultra-violet lines.

Thallium, on the other hand, resembles the alkali metals in giving lines in the ultra-violet at λ 353 and 378. C. H. B.

Leclanché Battery. By A. Ditte (*Compt. rend.*, **116**, 984—986).—When the zinc platinum couple is immersed in a solution of ammonium chloride (compare this vol., ii, 355), not only is the solution decomposed and the zinc oxidised, but the zinc oxide can act on the alkali chloride. At the ordinary temperature, the decomposition is more rapid the stronger the ammonium chloride solution. Hydrogen is evolved and compounds are formed which contain zinc oxide and ammonia in proportions that depend on the concentration of the solution. Apart from secondary reactions, the decomposition of ammonium chloride by zinc is exothermic. No precipitate is formed, because the zinc oxide is soluble in ammonia solution, but ammonia tends to accumulate in the upper part of the liquid and zinc chloride in the lower layers. The resistance is lessened, and decomposition accelerated by substituting for the plate of platinum a porous cell containing a mixture of carbon and manganese peroxide. With a solution containing 10 per cent. of ammonium chloride, the secondary product is $2NH_4Cl,4ZnO,9H_2O$, which crystallises as soon as the solution is saturated. When only a small quantity of ammonium chloride remains, zinc oxide separates and mixes with the crystalline compound. If the original solution contains 15 per cent. of ammonium chloride, the crystalline product is $2NH_4Cl,ZnO$, which tends to separate at first in the upper part of the liquid. In the lower part of the liquid there is very little free ammonia, and a double zinc ammonium

chloride is formed, and by reason of its specific gravity tends to remain at the bottom of the vessel, and thus accelerate the solvent action on the lower part of the zinc. C. H. B.

A Cadmium and Ammonium Chloride Battery. By A. Ditte (*Compt. rend.*, **116**, 1128—1131).—The electrolysis of a solution of ammonium chloride by a cadmium platinum couple is exothermic, even when the heat of formation of the double ammonium cadmium chloride is left out of account. The ammonia tends to accumulate in the upper part of the liquid and the cadmium chloride in the lower part, but since cadmium oxide forms most rapidly where the ammonia is present, the upper part of the liquid becomes saturated with the compound $2NH_4Cl,CdO$, which crystallises at the surface.

The substitution of an agglomerate of manganese peroxide, or a porous cell containing the peroxide, for the platinum, accelerates the change, and a layer of crystals of the compound $2NH_4Cl,CdO$ forms round the upper part of the zinc rod. The cadmium chloride tends to accumulate in the lower part and the ammonia in the upper part of the liquid, but at some intermediate point the two products are present in the proportions required to form the compound $2NH_4Cl,CdO$, and the latter separates out gradually, forming a kind of diaphragm dividing the liquids into two parts of different composition. Since, however, in this layer the resistance is smaller than in any other part of the liquid, the cadmium is more rapidly attacked at this point than anywhere else.

The manganese peroxide seems to have no other function beyond that of rapid depolarisation. C. H. B.

Voltaic Cells with Fused Electrolytes. By J. Brown (*Proc. Roy. Soc.*, **52**, 75—91).—In instituting a comparison of the observed electromotive forces of cells with their theoretical values, as given by "Thomson's law," the simpler the construction of the cell, the easier it is to ascertain the nature of the chemical action, on which the calculation rests. In cells with aqueous electrolytes, the solvent introduces several irreducible complications, arising from possible action of the solvent itself as an electrolyte, from the formation of insoluble films (either inactive and protective, as oxides, or active, as hydrogen) or from the uncertainty of calculations involving heats of solution of the products of voltaic reaction.

When the liquidity of the electrolyte is produced by fusion instead of by dissolution, these complications are to a large extent avoided; and, as a matter of experiment, two fluid cells made up of metals, immersed each in its fused chloride, give results nearer the "theoretical" values than those obtained with aqueous solutions. This is specially noticeable in the case of metals with high heats of oxidation, for example, magnesium and aluminium.

The electromotive forces of cells containing pairs of the metals tin, lead, and zinc come out nearest to the theoretical values. The other metals which were tried did not give so close an agreement, but could be brought into agreement by applying constant corrections, one for each metal; and reasons are given for attributing these corrections to

the high temperatures of the cells, as compared with the temperatures for which the recognised heats of combination are true.

Four of the cells were tested by passing currents through them in both directions alternately, and noting the electromotive force after the passage of each current. Polarisation was observed in the case of zinc-silver; in the others it was practically absent. J. W.

Changes at the Boundary between Solutions of Different Concentration during the Passage of an Electric Current. By G. H. Zahn (*Ann. Phys. Chem.* [2], **48**, 606—624).—The author has investigated the phenomenon of the separation of precipitates at the boundary of electrolytes (compare Kümmell, Abstr., 1892, 1038). The current was allowed to pass through two solutions of the same salt of different concentrations, from that of the greater to that of the less, a separation of the hydroxide of the metal then taking place at the boundary of the two solutions in certain cases. Such a separation was noticed with salts of magnesium, calcium, barium, strontium, aluminium, manganese, iron, zinc, and copper, but not in the case of silver salts. In the latter case, however, as also with the salts of sodium and potassium, which form soluble hydroxides, the presence of the hydroxides at the boundary between the solutions could be rendered evident by the alkaline reaction of the solution with methyl orange at this point. The author is inclined to regard the above phenomena as evidence that water plays some part in the electrolysis of salt solutions. H. C.

Electrochemical Effects on Magnetising Iron. By T. Andrews (*Proc. Roy. Soc.*, **52**, 114—117).—Two steel bars were cut adjacently from a long, finely-polished rod, so that they were as nearly as practicable alike in general composition and structure. Both were weighed and immersed in equal quantities of cupric chloride solution, one of them being previously magnetised. After a certain time (6 to 24 hours) they were removed from the solution, freed from deposited copper and carbonaceous matter, dried, and again weighed. In every case, the magnetised bar had lost more in weight than the unmagnetised bar, an average of 29 experiments showing an increase of corrosion in the steel due to magnetic influence of about 3 per cent. under the conditions of experiment. The bars were not highly magnetised. J. W.

Law of Dulong and Petit. By F. Richarz (*Ann. Phys. Chem.* [2], **48**, 708—716).—The author gives a deduction of the law of Dulong and Petit based upon the Clausius virial theory. H. C.

Specific Heat of Boron. By H. Moissan and H. Gautier (*Compt. rend.*, **116**, 924—928).—Pure amorphous boron was used, and it was mixed with small, lenticular masses of platinum with a view to increase the conductivity. The experiments were made with an ice calorimeter, and the following values were obtained:—At 100°, 0·3066; at 192·3°, 0·3407; and at 234·3°, 0·3573. The curve representing these results is almost a straight line, and the mean value

between 0° and 100° is 0·3066; between 100° and 192·3°, 0·3776; and between 192·3° and 234·3°, 0·4333. The corresponding atomic heats are 3·372, 4·153, and 4·766.

The mean specific heat between 0° and 100° is higher than that found by Weber, but the corresponding atomic heat is only 3·372. The specific heat, however, rises with the temperature, and extrapolation indicates that the atomic heat would be 6·4 at about 400°.

C. H. B.

Ferric Chloride and Ferric Oxalate Solutions: Distribution of Ferric Iron between Hydrochloric and Oxalic acids. By G. LEMOINE (*Compt. rend.*, **116**, 880—882).—When a solution of ferric chloride containing 4 gram-atoms of iron per litre is diluted with water, there is considerable development of heat, which, however, cannot be due to hydration, because it is observed on dilution of a solution containing $Fe_2Cl_6 + 108H_2O$. The development of heat is due to the gradual decomposition of the ferric chloride with formation of hydrochloric acid and soluble ferric hydroxide. This view is confirmed by colorimetric observations, by means of which the amount of alteration can be estimated. The following table shows the percentage alterations at various degrees of dilution. N represents a degree of concentration corresponding with a solution containing 56 grams of iron per litre.

	4N.	3N.	1·5N.	N.	½N.	¼N.	$\frac{1}{10}$N.
Percentage amount of ferric chloride undecomposed	100	74	50	46	37	35	29

The development of heat on dilution is much less marked with solutions of other ferric salts. At the ordinary temperature, dilution of ferric oxalate solution is accompanied by a slight absorption of heat, but if dilution takes place at about 80°, there is a slight development of heat.

The heat of formation of ferric oxalate from ferric oxide and oxalic acid is 34·8, but in concentrated solutions it is somewhat lower.

Oxalic acid to a large extent displaces hydrochloric acid when added to a solution of ferric chloride. C. H. B.

Decomposition of Oxalic acid by Ferric Salts under the influence of Heat. By G. LEMOINE (*Compt. rend.*, **116**, 981—983).—When ferric chloride and oxalic acid in equal molecular proportions are dissolved in water and heated, decomposition is insignificant at 40—50°, slow at 100°, but rapid in sealed tubes at 120°. At the ordinary temperature, only 0·019 of the mass was decomposed after six years. Water accelerates the decomposition, but the influence of dilution diminishes somewhat with the temperature. Excess of oxalic acid retards the change, but excess of ferric chloride accelerates it. Ferric sulphate and oxalic acid behave in a similar manner, but decomposition is somewhat slower, and the acceleration produced by water is much less marked.

Ferric oxalate in solution decomposes at 100° with separation of

ferrous oxalate. The velocity of the reaction at 100° is represented by the equation

$$\frac{d\frac{y}{p}}{dt} = a\left(1-\frac{y}{p}\right)^n = 0{\cdot}47\left(1-\frac{y}{p}\right)^{4{\cdot}4},$$

and it is noteworthy that the initial velocity, 0·47, is greater than in the case of ferric chloride and oxalic acid. When hydrochloric acid is added, the velocity approaches that of mixtures of ferric chloride and oxalic acid; and with a large proportion of the acid the reaction is almost arrested. Excess of water accelerates the change somewhat, but oxalic acid retards it.

The phenomena observed depend to a large extent on the decomposition of ferric salts by water, and the reverse action produced by the free acid present. C. H. B.

Some Applications of Raoult's Law at the Boiling Point of Solutions. By A. P. Paříźek and O. Šule (*Ber.*, **26**, 1408—1412). —The molecular weights of several of the fatty acids and their ethereal salts were determined from the boiling points of their solutions in benzene. In the case of the acids, the molecular weight obtained increases with the concentration of the solution, and eventually approximates to double the ordinarily accepted value. The ethereal salts give normal values in dilute solutions, the agreement being closer the higher the boiling point of the salt in question.

Water added to boiling alcohol causes first of all a depression and not a rise in the boiling point. The change Δt in the boiling point can be very well represented as a quadratic function of the percentage P of water in the alcohol $\Delta t = -0{\cdot}0411P + 0{\cdot}004348P^2$.

Rhamnose dissolved in alcohol gave a mean molecular weight of 206. This value points to the formation of an ethoxide, since $C_6H_{13}O_6Et = 210$, but $C_6H_{14}O_6 = 182$. The molecular weight of rhamnose was also determined from its effect on the boiling points of methyl and isopropyl alcohols. It was necessary, in the first place, to determine the molecular rise in the boiling points of these two liquids, for which experiments were made with benzaldehyde, aniline, and dimethylaniline. The values found were for methyl alcohol 9·20°, and for isopropyl alcohol 12·9°. Rhamnose gave in methyl alcohol solution a molecular weight 206, but in solution in isopropyl alcohol only 182. It appears, therefore, to form a methoxide, but no compound with isopropyl alcohol.

Water added to methyl alcohol causes only a rise in the boiling point. The molecular weight calculated from this is, however, abnormal, and lies between 31 and 37. Ethyl and isopropyl alcohols also give abnormal molecular weights in methyl alcohol solution. The value found for ethyl alcohol was between 110 and 118, and for isopropyl alcohol between 93 and 99. The formation of such molecular compounds as $EtOH,2MeOH = 110$ and $Pr^{\beta}OH,MeOH = 92$ is probable. H. C.

Coefficients of Affinity of Organic Bases. By E. LELLMANN and A. GÖRTZ (*Annalen*, **274**, 121—141).—A continuation of previously published work (Abstr., 1889, 1104; 1891, 638 and 1149). The values obtained with aniline both in more concentrated and more dilute solutions than previously used agree well, and the mean value is $\kappa = 67{\cdot}5$. The observation that freshly prepared solutions give a value either too high or too low is confirmed; it may be due to the equilibrium between the four substances in solution not being immediately established, and to alterations brought about by external agencies (such as the formation of molecular aggregates) not yet known. The following mean values were obtained with other bases: Metaxylidine, $\kappa = 106{\cdot}7$; paraxylidine, $\kappa = 72{\cdot}79$; ortho-xylidine, $\kappa = 96{\cdot}64$; ψ-cumidine, $\kappa = 117{\cdot}6$; orthotoluidine, $\kappa = 51{\cdot}63$; hexahydroquinoline, $\kappa = 59{\cdot}76$; decahydroquinoline, $\kappa = 618{\cdot}7$; ac.-tetrahydro-β-naphthylamine, $\kappa = 110{\cdot}5$; metachloraniline, $\kappa = 20{\cdot}85$; chlorotoluidine [$NH_2 : Cl : Me = 1 : 2 : 4$], $\kappa = 18{\cdot}53$; chlorotoluidine [$NH_2 : Cl : Me = 1 : 4 : 2$], $\kappa = 32{\cdot}26$; chlorotoluidine [$NH_2 : Cl : Me = 1 : 3 : 4$], $\kappa = 38{\cdot}54$; orthobromaniline, $\kappa = 12{\cdot}91$; metabromaniline, $\kappa = 24{\cdot}87$; parabromaniline, $\kappa = 31{\cdot}34$; bromotoluidine [$NH_2 : Me : Br = 1 : 2 : 4$], $\kappa = 28{\cdot}48$; bromotoluidine [$NH_2 : Me : Br = 1 : 4 : 2$], $\kappa = 16{\cdot}72$; glycocine, $\kappa = 17{\cdot}56$; metamidobenzoic acid, $\kappa = 21{\cdot}04$; picolinic acid, $\kappa = 9{\cdot}75$; cytisine is a strong base, but gave results which varied widely; thiohydantoïn, $\kappa = 10{\cdot}58$; dimethylthiazole, $\kappa = 26{\cdot}17$; the compound

$$\begin{matrix} CH_2{\cdot}S \\ | \\ CH_2{\cdot}S \end{matrix}\!\!>\!C{\cdot}NH,$$

$\kappa = 263{\cdot}7$. Arranging the bases according to their increasing affinity coefficients, a series is obtained which deviates from that of Walker, whose determinations were made by the electrolytic method.

A. R. L.

Coefficients of Affinity of Organic Acids. By E. LELLMANN and J. SCHLIEMANN (*Annalen*, **274**, 141—156, 156—173).—Using the method previously described (Abstr., 1892, 1269), the authors have made measurements of the affinity coefficients of certain organic acids. Their results deviate from those of Ostwald obtained by the electrolytic method, but in support of them, it is urged that they indicate an unbroken diminution in the affinity from formic acid to caprylic acid. The following are the mean values: Normal butyric acid, $\kappa = 10{\cdot}47$; caproic acid, $\kappa = 8{\cdot}72$; caprylic acid, $\kappa = 7{\cdot}63$. According to Ostwald, isobutyric acid is a stronger acid than propionic; the authors have, however, obtained the value $\kappa = 8{\cdot}21$ as its affinity coefficient. Mandelic acid, $\kappa = 56{\cdot}67$; dipyridylcarboxylic acid, $\kappa = 44{\cdot}11$; phenylpyridinecarboxylic acid, $\kappa = 28{\cdot}96$; sorbic acid, $\kappa = 13{\cdot}02$; α-naphthoic acid, $\kappa = 21{\cdot}62$. When a solution of phenylacetic acid is neutralised with barium hydroxide and examined in the usual way, the values obtained for the affinity coefficient vary according to the length of time the solution has been made; crystalline barium phenylacetate gave immediately after dissolution a mean value $\kappa = 19{\cdot}68$, which remained constant after 18 days; the value

obtained for hydrocinnamic acid at the end of the same time was $\kappa = 13{\cdot}85$.

The authors have also made some determinations of the affinity coefficients of acids by a spectrophotometric method in aqueous solution, using potassium metahydroxyanthraquinonesulphonate as indicator. The results are at variance with Guldberg and Waage's law; water does not, therefore, appear to be a suitable solvent for these determinations. Contrary to the dissociation degrees, the differences between the values for the affinity coefficients become greater with increasing dilution. Another series of experiments, in which dimethylamidoazobenzenesulphonic acid in aqueous solution was employed as indicator, leads the authors to the view that the chemical action is not proportional to the dissociation degree. Ostwald, by comparing the rate of hydrolytic action of acids with their electrical conductivities, arrived at an opposite conclusion. Certain acids are arranged in the order of their increasing strengths according to the authors' and to Ostwald's results; the two tables exhibit very large differences. The authors also reply to Arrhenius' criticisms (*Zeit. physikal. Chem.*, **10**, 671) of their former work.

A. R. L.

Theory of Chemical Types. By F. Flavitzky (*Ber.*, **26**, 1534—1538).—This paper adduces further evidence in favour of the author's theory of the correlation of the oxygen and hydrogen compounds of the elements (Abstr., 1892, 1270). It is shown that the general type represents all the compounds of the elements, including the so-called molecular compounds, this being especially evident in the case of the halogen derivatives, such as the single and double haloïd salts, with their water of crystallisation. H. G. C.

Lectures on Inorganic Chemistry arranged in accordance with the Natural System of the Elements. By L. Meyer (*Ber.*, **26**, 1230—1250).—In a lecture before the German Chemical Society, the author explains how, for some years past, he has made use of the periodic system in giving instruction in inorganic chemistry. He claims that the advantages obtained by making use of this method of classification are so great that he is now able to cover the whole of the ground in little more than 80 lectures, in spite of the fact that these are very fully illustrated by experiments.

The course commences with an explanation of the position occupied by chemistry among the other sciences, and of its relationship to these, and more especially to physics. A short historical account of the progress of chemistry follows, this being brought down to the time of Lavoisier, and serving to introduce an examination into the composition of air and of the nature of combustion. In connection with the phlogiston theory, hydrogen is brought forward, and the composition of water made the subject of investigation. The constancy in the combining proportions of hydrogen and oxygen by weight and by volume is exemplified, and the student in this way becomes acquainted with the eudiometer and with decomposition by electrolysis. The atomic theory is also briefly spoken of in this place. The elements oxygen, nitrogen, and hydrogen having been thus intro-

duced, the elements generally are spoken of, together with their distribution in Nature and relative importance. The laws in accordance with which they enter into combination with one another are considered at some length, the atomic theory being brought forward historically, and the laws of Dulong and Petit, and of Avogadro, are fully discussed. At the same time the historical treatment permits of the introduction of the electrochemical theory, in speaking of electrochemical equivalents and Faraday's laws of electrolysis.

The meaning of atomic weights being now rendered evident, the arrangement of the elements in the periodic system is at once explained. The author then starts with a consideration of the compounds of hydrogen with the elements, beginning first with those of Group VII, this serving to illustrate practically the similarity to be looked for in analogous compounds of elements belonging to the same group, and also the regular change in valency in passing from one group to the next. After these preliminaries, the elements and their compounds are considered *seriatim*, commencing with Group I in the periodic system. It is considered advisable, however, in dealing with the elements in this manner, to reserve the heavy metals in the first four groups to be discussed at a later period, the sub-groups being first alluded to when Group V is reached, and then subsequently taken in the following order:

V.	VI.	VII.	VIII.	I.	II.	III.	IV.
V,	Cr,	Mn,	Fe, Co, Ni,	Cu,	Zn,	Ga,	Ge,
Nb,	Mo,	—	Ru, Rh, Pd,	Ag,	Cd,	In,	Sn,
Ta,	W,	—	Os, Ir, Pt,	Au,	Hg,	Tl,	Pb.

Under the headings of the metals only those compounds are considered which may be regarded as derived from the hydrogen compounds previously spoken of, as, for instance, the oxides, sulphides, and chlorides. Salts of the oxy-acids are taken when the acid itself is under discussion, the author being inclined, from practical experience, to look on this as the better method of treatment, and one by means of which useless repetition may be avoided.

H. C.

Explosives. By H. Biltz (*Ber.*, **26**, 1378—1383).—There are certain explosives, such as nitroglycerol, dynamite, guncotton, picric acid, and the new German military powder, which, when simply heated, burn quietly if freely exposed, or, if confined, explode only at the spot where heat is applied without the whole mass taking part in the explosion. This is probably because they are bad conductors of their own explosive wave. If, however, the same substances are subjected to a violent shock by the explosion in their midst of initial charges of mercury fulminate, the shock seems to affect all the molecules of the explosive at once, and the whole mass of the latter explodes with enormous violence.

Descriptions are given of lecture experiments to illustrate these phenomena.

C. F. B.

Inorganic Chemistry.

Densities and Molecular Volumes of Chlorine and Hydrogen Chloride. By A. Leduc (*Compt. rend.*, **116**, 968—970).—The hydrogen chloride was prepared by the action of concentrated sulphuric acid on fused sodium chloride, and dried over phosphoric anhydride; its density is 1·2696, and its molecular volume (oxygen = 1) is 0·9923.

The chlorine was obtained from a vessel of liquefied chlorine, a part of which had previously been allowed to evaporate. Hydrogen chloride was removed by means of cupric sulphate, and the chlorine was dried over concentrated sulphuric acid. Its density is 2·4865, and its molecular volume 0·9854.

The values in both cases differ considerably from those usually given. C. H. B.

Combination of Oxygen and Hydrogen. By H. N. Warren (*Chem. News*, **67**, 195).—1 c.c. of acidified water was introduced into small, selected glass tubes $1\frac{1}{2}$ inches long, into one end of which two platinum wires were fused, whilst the other end was sealed up. When these were subjected to the action of an electric current of 6 volts, the tubes rapidly burst owing to the heating of the liquid; when, however, one of the tubes was mounted within a strong glass vessel containing water, the action continued briskly for 25 minutes, when a vivid flash and violent explosion terminated the experiment. The author infers from many such experiments that under a pressure of 180 atmospheres free oxygen and hydrogen combine with great violence without the application of flame. D. A. L.

Gravimetric Composition of Water. By W. Dittmar and J. B. Henderson (*Chem. News*, **67**, 127, 139—141, 151—152, 164—167).—The authors have submitted the synthesis of water by the action of hydrogen on copper oxide to two series of rigorous quantitative experiments. Specially devised, accurately adjusted, and duly tested apparatus was employed, which could be securely sealed air-tight by stop-cocks and india-rubber caps and stoppers. The mode of procedure was to charge the tube in which the reduction was to take place with about 115 grams of copper oxide, to heat it on a magnesia bath in a current of dry air, using about 4·5 litres, then to close it securely, and the next day exhaust it, admit hydrogen into it, allow it to assume the temperature of the balance case, exhaust again, measuring the vacuum, and weigh against a tare, prolonging the weighing so as to insure that no leakage of air was taking place, the exposed portions of india-rubber being protected by very thin silver foil during the weighing. The tube is then placed on a magnesia bath, and the water receptacle and various U-tubes adjusted; every trace of air is then eliminated by passing several litres of hydrogen through the cold apparatus, and the portions of the reduction tube which are not to be heated being properly protected, the heating is now proceeded

with, when the conversion into water ensues below redness; the water receptacle during the formation of water is immersed in an ice bath, which is replaced by a water bath at the temperature of the laboratory as soon as the copper oxide appears completely reduced, after which period the experiment is continued for a while to make certain that the reduction is quite complete; ultimately the apparatus is allowed to cool in a current of hydrogen before being detached. When detached, the hydrogen in the various pieces of apparatus is replaced by air dried by sulphuric acid; the tubes, &c., are then securely closed and weighed. The various weighings incidental to an experiment in the first series of syntheses were:—Reduction tube + copper oxide, reduction tube + copper, water flask before and after experiment, 1st U-tube, 2nd U-tube (sulphuric acid), and 3rd U-tube (phosphoric anhydride), both before and after; the last tube was found to be practically superfluous. From these weighings were deduced: the weight of oxygen consumed; the weight of water obtained, and the weight of hydrogen with which the oxygen had combined. These data were corrected for sulphurous anhydride carried in the hydrogen from the sulphuric acid used for drying the gas, and which amounted to less than 0·2 milligram per litre; for the air displaced by the water, copper, and copper oxide, taking the mean gravity of the former at 8·7016, and of the latter at 6·1418, whilst the composition of the latter, although not constant, was found to be in a sample O + 1·0985Cu, a number which was adopted for these calculations; and for the oxygen absorbed by the metallic copper when replacing the hydrogen in the reduction tube by dry air before weighing.* The methods of ascertaining the magnitude of these corrections are fully described in the paper.

After the authors had become aware of various sources of error, the second series of syntheses were started, in which hydrogen absolutely free from oxygen is employed, this being prepared by passing the gas (after its deoxidation by red-hot copper) over fused caustic potash, followed by phosphoric anhydride. These reagents placed in the same order after the water receptacle served to absorb the water vapour produced during the second series of experiments; therefore in this series there were only two U-tubes to weigh. Of course the purity of the water obtained was duly established. The authors discuss the results obtained very fully, and, excluding results in which there were irregularities in the experiments, they find that the amount of hydrogen required by 8 grams of oxygen equalled in 10 experiments 1·00879 grams, and in the seven best experiments 1·00848 grams, and they therefore adopt for the atomic weight of hydrogen H = 1·0085 (O = 16), or O = 15·866 or 15·87 (H = 1), as the net result of their work.

The paper concludes with a summary of the work of previous investigators on this point. The atomic weight of hydrogen (O = 16) was found to be 1·0075 by Stas, 1·0083 by Cooke and Richards, 1·0072 by W. A. Noyes, 1·0069 by Lord Rayleigh, and 1·0032 by E. H. Keiser.

D. A. L.

* In some instances a correction for occluded hydrogen is made.

Production of Hydrogen Peroxide during the Spontaneous Oxidation of Zinc: Combustion by Oxygen. By M. TRAUBE (*Ber.*, **26**, 1471—1475).—The author has already shown (Abstr., 1885, 1105) that small quantities of hydrogen peroxide are formed by the slow oxidation of zinc and other metals. This fact leads him to the view that during the slow oxidation of zinc, the water, and not the oxygen, is dissociated. The reaction may be represented as taking place in two stages (1) $Zn + 2H_2O + O_2 = Zn(OH)_2 + H_2O_2$; (2) $Zn + H_2O_2 = Zn(OH)_2$.

Schoenbein found that by shaking lead amalgam with very dilute sulphuric acid and air for 10 seconds, 95—98 per cent. of the theoretical amount of hydrogen peroxide was obtained, whilst at the end of 100 seconds only about half this amount was present. The following method was devised by the author in order to arrest the decomposition of the hydrogen peroxide as soon as it is formed. 500 c.c. of 3 per cent. milk of lime containing 1·33 per cent. of potash, 70 grams of mercury, and 10—20 milligrams of zinc in coarse powder previously amalgamated on the surface, are shaken together in a closed flask with air freed from carbonic anhydride. The zinc dissolves at first, then reprecipitates, and finally liquefies. As soon as this occurs, more zinc is added (16—20 milligrams at most) from time to time. In this way, all the hydrogen peroxide is precipitated as calcium peroxide, and its amount may, after acidifying a portion of the liquid, be ascertained by titration with permanganate. Similar results are obtained with barium or strontium hydroxides instead of calcium hydroxide, and with cadmium instead of zinc. This result is in accord with the author's electrolytic synthesis of hydrogen peroxide (*Sitzungsber. Akad. Berlin*, 1887, 1048). The hydrogen at the cathode immediately combines with the oxygen of the air, forming hydrogen peroxide, which is reduced to water by a further quantity of hydrogen. The difference is merely that in one case hydrogen is produced by the agency of zinc, and in the other by that of the electric current.

The observations of Dixon and of Baker that phosphorus, carbonic oxide, and carbon are only combustible in oxygen when water is present seem also to show that no dissociation of oxygen takes place, but that water when present undergoes decomposition. As a matter of fact, the author has shown (Abstr., 1885, 1108) that the carbonic oxide flame contains hydrogen peroxide. The question whether the oxidation of hydrogen gas at a high temperature requires the presence of water must be left undecided for the present; at any rate, dissociation of oxygen occurs, for considerable quantities of hydrogen peroxide are present under certain circumstances in the hydrogen flame.

The author states, in conclusion, that hydrogen peroxide is only formed when oxidation is brought about by ordinary oxygen. Other oxidising agents (ozone excepted, see next abstract) do not give rise to the production of hydrogen peroxide. Palladium hydrogen, for example, in the presence of air and water yields hydrogen peroxide, whereas with permanganate solution water is formed directly. Compare Armstrong (Proc., 1893, 145, *et seq.*). A. R. L.

Constitution of Hydrogen Peroxide and of Ozone. By M. TRAUBE (*Ber.*, **26**, 1476—1481).—In the first portion of this paper the author upholds his view (Abstr., 1886, 660) that hydrogen peroxide is a compound of 1 molecule of oxygen with 2 atoms of hydrogen. Hydrogen peroxide acts as an oxidising agent only towards powerfully reducing substances, such as zinc and sulphurous anhydride, with which it unites as $(OH)_2$. Schoenbein states that it does not react immediately with phosphorous acid or phosphorus, Weltzien found that a solution of hydrogen peroxide placed over phosphorus did not alter in titre after two months, and, according to Lustig, hydrogen peroxide has no action on alcohol, even in presence of dilute sulphuric acid. Hydrogen peroxide, in a very dilute solution, only slowly liberates iodine from potassium iodide, and the author finds that it does not oxidise normal potassium oxalate, even when boiled with it. If hydrogen peroxide consisted of two hydroxyl groups, it ought to be obtained by the electrolysis of barium hydroxide, but no trace of it appears at the anode, only active (atomic) oxygen.

Hydrogen peroxide and ozone are closely related, and the author assigns the formulæ "2H.O=O" and "O.O=O" to them respectively. In support of this formula for ozone, it is urged that in its reactions only 1 atom of oxygen is active, the others being evolved as ordinary oxygen.

Potassium tetroxide is a reducing agent towards acid solutions of permanganate, and decomposes directly into hydrogen peroxide when treated with acid without giving rise to active oxygen, for, if the decomposition takes place in the presence of indigosulphonic acid, the latter remains unaltered. The author therefore represents it thus, "K.O=O.O=O.K."

The author has already elsewhere proposed the name holoxides for compounds of the type of hydrogen peroxide. A. R. L.

Sulphuryl Peroxide (Holoxide). By M. TRAUBE (*Ber.*, **26**, 1481).—By repeating his former experiments (Abstr., 1891, 978), the author has obtained products which, on reduction, gave a ratio of active oxygen to sulphuric anhydride = 1 : 10, indicating ordinary persulphuric acid. It may be assumed from this that the compound SO_4 is only obtained when conditions are obeyed which have not at present been ascertained; its existence cannot for the present be insisted on. A. R. L.

Conditions of the Formation and Decomposition of Nitrous acid. By V. H. VELEY (*Proc. Roy. Soc.*, **52**, 27—54).—The formation of nitric peroxide, which imparts the yellow tint to nitric acid, takes place in concentrated acids even at 30°, but with moderately dilute acids only at 100—150°, when the acid is not unduly exposed to sunlight.

The reaction between nitric oxide and nitric acid may be regarded as reversible, thus, $2NO + HNO_3 + H_2O \rightleftarrows 3HNO_2$, when the solution is sufficiently dilute and the temperature low. For equilibrium, the ratio of the quantities of nitric and nitrous acids is about 9 : 1. With more concentrated acids, and at higher temperatures, the

chemical changes taking place are more complicated. In solutions containing both nitric and nitrous acids, the rate of change at any moment is proportional to the mass of the nitrous acid present, and is dependent on the ratio of the masses of nitrous and nitric acid, being the more rapid the greater the proportion of the former to that of the latter. In the particular case of the liquids prepared from nitric oxide and nitric acid, the rate of change was found to vary with the temperature according to the equation $v_t = vk^{t-t_1}$.

Nitrous-nitric acid solutions prepared in different ways behave in a similar manner as regards the diminution of the mass of the nitrous acid, but in other respects, such as the evolution of gases and action on metals, they are dissimilar. J. W.

Graphite. By W. Luzi (*Ber.*, **26**, 1412—1414; compare Abstr., 1892, 406, 565, 945; and this vol., ii, 320).—Previous to the author's observation of the fact it was not known, as is implied in a statement of Moissan's (this vol., ii, 320), that there are certain varieties of graphite ("graphitite") which do not swell up when ignited with nitric acid.

Graphite from ordinary cast iron has been observed to swell up when ignited with nitric acid, although not in so marked a degree as in some other cases. C. F. B.

Rubidium Salts: a Correction. By W. Muthmann (*Ber.*, **26**, 1425—1426).—For "$RbSbCl_4$ and $CsSbCl_4$" (this vol., ii, 321) read "$3RbCl,2SbCl_3$ and $3CsCl,2SbCl_3$." C. F. B.

Fluorides of the Alkaline Earths. By C. Poulenc (*Compt. rend.*, **116**, 987—989).—Strontium chloride is decomposed by hydrogen fluoride at the ordinary temperature, with formation of an amorphous fluoride which only becomes indistinctly crystalline when heated in hydrogen fluoride at 1200°. Even at this temperature it does not volatilise.

Amorphous strontium fluoride is insoluble in cold water and almost insoluble in hot water; it is completely dissolved by boiling hydrochloric acid, but is much less easily attacked by nitric acid. Sulphuric acid converts it into strontium sulphate, and when heated in the air at 1000°, it is partially converted into the oxide. Hydrogen chloride decomposes it at a red heat, but water vapour or hydrogen sulphide is without action at this temperature. Alkali carbonates decompose it in the ordinary way. Its sp. gr. is 2·44.

When the amorphous fluoride is fused with alkali chlorides, it crystallises in octahedra, but is partially decomposed. When fused with potassium hydrogen fluoride, there is no decomposition, but the crystals are not so well defined. A mixture of equal parts of potassium hydrofluoride and potassium chloride, however, gives beautiful, transparent, regular octahedra. Strontium chloride, when fused with potassium hydrofluoride, yields simply crystallised strontium fluoride.

Barium fluoride is obtained in beautiful octahedra by fusing the

amorphous fluoride with potassium hydrofluoride and potassium chloride. Potassium chloride alone partially decomposes the barium fluoride with the formation of double salts. C. H. B.

Lead Tetrachloride. By H. Friedrich (*Ber.*, **26**, 1434—1436; compare Abstr., 1890, 699; also Classen and Zahorski, *Zeit. anorg. Chem.*, **4**, 100).—When lead dichloride is suspended in hydrochloric acid and gaseous chlorine passed into the liquid, a solution of lead tetrachloride is obtained, from which, on addition of ammonium chloride, a compound, $PbCl_4,2NH_4Cl$, analogous to ammonium stannichloride, separates. If this compound is added to concentrated sulphuric acid, an energetic reaction ensues, and *lead tetrachloride* separates as an oily substance; it is purified by shaking with fresh quantities of sulphuric acid. In the pure state, it is a translucent, yellow, highly refractive liquid which fumes in contact with moist air, with decomposition into lead dichloride and chlorine; it may be kept under cold concentrated sulphuric acid, but when heated with it, it decomposes with explosion into lead dichloride and chlorine. When, however, lead tetrachloride is heated in a retort with concentrated sulphuric acid, and a current of chlorine passed through, a certain quantity of the tetrachloride distils over below 105°, at about which temperature explosion occurs. The sp. gr. of lead tetrachloride at 0° is 3·18, and it solidifies to a yellowish, crystalline mass at −15°; it forms a hydrate in the presence of a little water, which, by the further addition of water, decomposes into lead peroxide and hydrogen chloride; when brought in contact with a small quantity of cooled hydrochloric acid, a crystalline derivative, probably $PbCl_4,2HCl$, is formed.

When ammonium stannichloride is added to concentrated sulphuric acid, stannic chloride is precipitated, and may be distilled over. Further details of these and other experiments will appear in the *Monatsheft*. A. R. L.

Ternary Alloys. Part VI. By C. R. A. Wright (*Proc. Roy. Soc.*, **52**, 11—27; compare this vol., ii, 15).—In this paper, the author studies alloys containing aluminium in place of the zinc used in the mixtures previously described. The aluminium employed contained considerable quantities of impurity, chiefly silicon and iron, which found their way almost entirely into the lighter alloy.

In the case of mixtures of aluminium, lead, and tin, the ratio of tin and lead in the heavier alloy, where the difference between the percentages of tin in the two layers is greatest, corresponds nearly with the formula $SnPb_3$. At the temperature of experiment, about 800°, the aluminium alloy contained 1·91 per cent. of lead, and the lead alloy 0·07 per cent. of aluminium. The composition at the limiting point was: lead, 19·4; aluminium, 18·0; and tin, 62·6.

For mixtures of bismuth, aluminium, and tin at 650°, the composition at the limiting point was 18·6, 25·6, and 55·8 per cent. of these metals respectively. The bismuth contained 0·28 per cent. of aluminium, and the aluminium alloy 2·02 per cent. of bismuth when no tin was present.

The limiting alloy for aluminium, lead, and silver contained 40 per cent. of lead, 1·75 per cent. of aluminium, and 58·25 per cent. of silver at 870°. No indications of the existence of a compound of aluminium and silver were obtained. At the same temperature, the limiting composition for bismuth-aluminium-silver alloys, was bismuth, 39·5 per cent.; aluminium, 2·25 per cent.; and silver, 58·25 per cent., representing a ratio between bismuth and aluminium near to that indicated by the formula $AlBi_2$. J. W.

Basicity and Functions of Manganous acid. By G. Rousseau (*Compt. rend.*, **116**, 1060—1062).—In its compounds with barium and strontium, BaO,MnO_2 and SrO,MnO_2, manganous acid seems to be bibasic, but in the saline oxide, $2MnO,MnO_2$, and the calcium compound, $2CaO,MnO_2$, it seems to be tetrabasic. The author has made experiments with a view to determine the influence of the alkalinity of the mixture on the composition of the manganites formed in it.

Calcium chloride is fused at an orange-red heat and mixed in successive small quantities with about one-fifth of its weight of precipitated calcium carbonate. When evolution of carbonic anhydride ceases, the temperature is lowered to the melting point of copper, and dried manganous chloride is added. Under these conditions, long needles of the manganite $CaO,2MnO_2$ form rapidly. After heating for an hour, the crucible is raised to an orange-red heat, and the contents well stirred and again heated for 30 or 40 minutes. Short, brilliant, black prisms of the manganite CaO,MnO_2 are thus obtained. This compound dissolves readily in strong hydrochloric acid, but is not attacked by dilute nitric acid, and differs in this respect from the manganite $2CaO,MnO_2$. It is formed in mixtures that contain from 3·24 to 2·56 mols. of calcium chloride for each mol. of the oxide. With from 2·0 to 2·5 mols. of the chloride to each mol. of the oxide, mixtures of CaO,MnO_2 and $2CaO,MnO_2$, in varying proportions, are obtained. With 1·92 mols. of the chloride to 1 mol. of the oxide, the compound $2CaO,MnO_2$ is obtained pure. It follows that the bibasic manganite ceases to be stable when the mixture contains 2 mols. of calcium chloride to 1 mol. of calcium oxide.

If the crucible is covered, the temperature of the surface of the fused mass rises, and needles of the dimanganite are obtained instead of the manganite. The zone of stability of the latter in fact lies between 1000° and 1100°, the dimanganite being formed above and below these limits. It seems, therefore, that calcium manganite undergoes the cycle of changes that characterises other manganites. When strontium manganite, SrO,MnO_2, is fused with strontium chloride, to which increasing quantities of strontium oxide are added, it changes progressively, and tends towards a limit corresponding with the bibasic manganite, $2SrO,MnO_2$.

It would seem that manganous acid is capable of behaving as a tetrabasic acid, but it has really only two acid functions, giving rise to salts of the type $M''O,MnO_2$, whilst the other two functions are more of the nature of alcoholic functions, and are active only in strongly basic media.

The existence of salts such as $2CaO,MnO_2$, derived from the unknown hydroxide $Mn(OH)_4$ affords further evidence that manganese is tetravalent. C. H. B.

Hydrates of Manganous Sulphate. By C. E. LINEBARGER (*Amer. Chem. J.*, **15**, 225—248).—The author describes the methods by which he has obtained manganous sulphate crystallising with 1, 2, 3, 4, 5, 6, and 7 mols. of water, and has determined the solubility of the seven hydrates, and of the anhydrous salt, in water. The salt has the property of uniting with water to form "crystallo-hydrates" between the temperatures −10° and +117°; below the former temperature, a mechanical mixture of the heptahydrate and ice separates out; above the latter temperature, only the anhydrous salt is capable of existence. As the amount of water of crystallisation in the hydrates seems in the main to depend on the temperature, this interval of 127° may be divided into seven intervals without any sharp lines of demarcation, to each of which one of the hydrates corresponds. The solubilities of the hexa-, penta-, tetra-, tri-, and di-hydrates do not increase so rapidly as the temperature, whilst the solubilities of the mono-hydrate and of the anhydrous salt diminish less rapidly than the temperature rises. Moreover, considering the hexa-, penta-, tetra-, and tri-hydrates, the more water of crystallisation the hydrate contains, the greater its solubility. The contrary is generally the case with the different hydrates of other salts examined up to date.

The heat of solution of the penta- and tetra-hydrates is undoubtedly negative, whilst their heat of dilution is positive. A solution of the sulphate containing 70 parts of anhydrous salt to 100 parts of water (the concentration of a saturated solution of the tetrahydrate at 20°), when exposed to the temperature of 25°, dissolves more of the tetrahydrate, with a slight absorption of heat, a result entirely in accordance with the law showing the relation of temperature to solubility, advanced by Le Chatelier and Van't Hoff. G. T. M.

Mineralogical Chemistry.

New Mineral from Boléo, Mexico. By E. CUMENGE (*Compt. rend.*, **116**, 898—900).—The copper deposit of Boléo, in Lower California, worked by a French company on a large scale, has already furnished a curious mineral species described in 1891, by Mallard and Cumenge, as boléite. The author has now discovered in the Soledad Valley a new mineral containing, like boléite, copper, lead, and chlorine, but in different proportions. The orthorhombic crystals are of a violet-blue colour, and have a sp. gr. of 4·67. Analysis gave results in accord with the formula $PbCl_2,CuO + 2H_2O$.

B. H. B.

Metacinnabarite from Idria. By A. SCHRAUF (*Jahrb. f. Min.*, 1893, i, Ref. 461—466; from *Jahrb. k. k. geol. Reichsanstalt*, **41**, 379—399).—In this exhaustive memoir, the author gives the results of a series of investigations of rocks and minerals from Idria. The most interesting mineral he describes is the black mercury sulphide, metacinnabarite, found in the Josefi workings at Idria. In a state of purity, this mineral has a sp. gr. of 7·66, and contains 85·62 per cent. of mercury and 14·09 per cent. of sulphur. B. H. B.

Arsenical Pyrites. By F. SCHERER (*Zeit. Kryst. Min.*, **21**, 354—387).—In this monograph on arsenical pyrites, the author gives a full bibliography of the subject, and the results of a crystallographical and chemical examination of arsenical pyrites from the following localities:—1. Freiberg (Himmelfahrt mine); 2. Macagão, Brazil; 3. Deloro, Ontario; 4. Thala Bisztra and Oravicza; 5. Turtmannthal, in Wallis; 6. Modum, in Norway; 7. Bieber, in Hessen; 8. Bräunsdorf, near Freiberg; 9. Munzig, near Meissen; 10. Rauris, in Salzburg; 11. Redruth, in Cornwall; 12. Pestarena, in Piemont; 13. Sala, in Sweden; and 14. Csiklova, in the Banat. Of the last seven, only crystallographical descriptions are given. At the conclusion of the paper, a tabular statement is given of the crystallographic form and chemical composition of all the varieties of arsenical pyrites that have been examined.

The chief conclusions to be drawn from the mass of information got together by the author are, that the arsenical pyrites are frequently not homogeneous compounds, but contain inclusions of magnetite and of other minerals, and that the axial ratio $a : b : c$ does not appear to be dependent on the percentage of sulphur the mineral contains.

B. H. B.

Hauchecornite, a Nickel-bismuth Sulphide. By R. SCHEIBE (*Jahrb. f. Min.*, 1893, i, Ref. 466—467; from *Jahrb. k. preuss. geol. Landesanst. für* 1891, 91—125).—This mineral was found in 1884, in spathic iron ore, at the Friedrich mine, in the mining district of Ham, on the Sieg. Hauchecornite is of a light, bronze-yellow colour, with a hardness of 5, and a sp. gr. of 6·4 On analysis, it yielded—

S.	Bi.	Sb.	As.	Pb.	Zn.	Fe.	Co.	Ni.
22·74	24·10	6·22	1·10	0·22	0·04	0·44	1·45	44·01

Its formula is $Ni_{14}SbBi_2S_{13}$. B. H. B.

Zirconiferous Felspathic Inclusion in Basalt. By F. GONNARD (*Compt. rend.*, **116**, 896—898).—A quarry opened some years ago on the south flank of the Montaudou peak, near Royat, has attracted the attention of geologists, who have examined the felspar inclusions in the basaltic rock. The author now describes a specimen of this felspar, enclosing several very fine zircons of a hyacinth-red colour. This is the first undoubted example of the existence of zircon in its usual matrix that has yet been met with in the Puy-de-Dôme.

B. H. B.

Phosphates from Florida. By H. J. Buisman and A. R. van Linge (*Rec. Trav. Chim.*, 286—289).—Four samples of phosphates from Florida have been analysed: I was soft, white, and had not been ignited; II, hard, white, ignited; III, hard, greenish-grey, marbled, ignited; IV, not ignited, otherwise like III.

	I.	II.	III.	IV.
H_2O (lost at 150°)....	0·77	0·76	0·63	1·10
CO_2	1·36	1·67	2·20	2·51
P_2O_5.....	32·49	36·61	34·99	35·57
$Fe_2O_3 + Al_2O_3$.....	2·60	2·65	2·70	1·70
F	3·29	3·40	3·40	3·16

The phosphoric acid, if all combined with calcium, corresponds with

$Ca_3(PO_4)_2$.....	70·92	79·98	76·37	77·64

No bromine could be detected, and only traces of chlorine.

C. F. B.

Phosphatic Rocks of Animal Origin and a New Type of Phosphorites. By A. Gautier (*Compt. rend.*, **116**, 928—933).—The Grotto of Minerva or La Coquille, in the extreme south-west of the Department of Hérault, contains yellowish-white, micro-crystalline *brushite*, $CaHPO_4,2H_2O$. The floors of the galleries consist of an earthy and concretionary phosphatic deposit of a thickness of at least 7 or 8 metres. This deposit contains flint implements, pottery, bronze ornaments, and other prehistoric remains, together with a large quantity of bones. One of the bones, a dorsal vertebra of a cave bear, had the composition CO_2, 2·264; SO_3, 0·283; P_2O_5, 34·790; Cl, 0·065; F, 0·853; Al_2O_3 (and traces, Fe_2O_3), 0·610; CaO, 44·590; MgO, 0·106; ZnO, 0·149; Pb, traces; silica and sand, 2·163; nitrogenous organic matter, 5·24; water lost at 170°, 8·78 = 99·893. It is noteworthy that the chlorine originally present in the bones has been to a great extent displaced by fluorine. The presence of zinc is probably due to the fact that the animals were fed in a district the soil of which contains zinc.

The deposit in which the bones are embedded varies in composition, but an average sample gave the following numbers on analysis:—Water lost at 120°, 5·81; loss at a red heat, 4·33; sand and ferruginous clay, 45·25; $CaSO_4$, 11·31; $CaCO_3$, 4·00; $Ca_3(PO_4)_2$, 17·45; $Al_2P_2O_8$, 10·63; CaF_2, 1·83; MgO, trace. C. H. B.

New Type of Phosphorites. By A. Gautier (*Compt. rend.*, **116**, 1022—1028).—In the Grotto of Minerva (preceding abstract), at a depth of 3 to 4 metres below the surface, there is a yellowish, hard, concretionary layer, from 5 to 9 metres thick, which follows the undulations of the underlying Devonian rock. This concretionary layer has the composition: water and organic matter, 17·18; SiO_2, 13·00; CaO, 16·24; Al_2O_3, 24·29; P_2O_5, 27·59; Mg, Fe, SO_4, traces; F, 2·104 = 100·404. The other phosphates found in the same deposit differ considerably in composition and in physical properties, some being

brittle, and even pulverulent, and some so light that they float upon the water, but they are alike in containing a considerable proportion of aluminium phosphate and so low a proportion of calcium that it is not sufficient to form tricalcium phosphate, nor even, in some cases, dicalcium phosphate. In this respect the phosphorites of the Grotto of Minerva differ from all ordinary phosphorites, the proportion of calcium in the latter being always sufficient to form tricalcium phosphate. The phosphorites in the grotto also contain a higher proportion of calcium fluoride.

The aluminium and calcium phosphates seem to be simply mixed, since the former dissolves readily in dilute solutions of alkalis, and ammonium citrate dissolves a much larger proportion of phosphoric acid than from ordinary phosphorites.

The only known double phosphates of aluminium and calcium are *tavistockite* and *cirrolite*, but both these are rare, and the deposit in the Grotto of Minerva is the first to yield the two separate phosphates, crystallised dicalcium phosphate and hydrated aluminium phosphate.

C. H. B.

Brandite and Friedelite. By G. Lindström (*Jahrb. f. Min.*, 1893, ii, Ref. 9—10; from *Geol. Fören. i Stockholm Förh.*, **13**, 123).—Brandite occurs with heavy spar, calcspar, caryopilite, and sarkinite in fissures in the Harstig mine, Sweden. Analysis gave the following results:—

As_2O_5.	P_2O_5.	PbO.	MnO.	FeO.	MgO.	CaO.	H_2O.	Cl.
50·48	0·05	0·96	14·03	0·05	0·90	25·07	8·09	0·04

The formula is therefore $2CaO,MnO,As_2O_5 + 2H_2O$. The mineral has a sp. gr. of 3·671. It crystallises in the triclinic system.

Red hexagonal crystals of friedelite are found at the same mine, with galena, specular iron ore, and augite in fissures filled with calcite. On analysis, they yielded the following results:—.

SiO_2.	FeO.	MnO.	CaO.	MgO.	Cl.	H_2O.	P_2O_5.
33·36	3·83	49·08	0·74	1·31	4·19	8·45	trace

The percentage of manganese oxide is somewhat too high, on account of admixed hausmannite.

B. H. B.

Adelite and Svabite, New Swedish Minerals. By H. Sjögren (*Jahrb. f. Min.*, 1893, ii, Ref. 38—39; from *Geol. Fören. i Stockholm Förh.*, **13**, 781).—A new basic arsenate from Nordmarken and Långban is termed by the author adelite (ἄδηλος, cloudy). It occurs in large masses with manganese minerals. Analysis gave results in accord with the formula $4RO,H_2O,As_2O_5$, in which R represents Ca, Mg, together with some Mn, Fe, Pb, Cu.

Svabite is a new mineral of the apatite group from the Harstig mine. Its composition is represented by the formula

$$3As_2O_5,10CaO,H_2O.$$

The chemical analogy with apatite is supported by the results of the crystallographical examination.

B. H. B.

Långbanite. By H. SJÖGREN (*Jahrb. f. Min.*, 1893, i, Ref. 471—472; from *Geol. Fören. i Stockholm Förh.*, **13**, 256).—The author has continued, on material recently obtained at Långbanshyttan, his former researches, and finds that the hexagonal tablets in finely granular schefferite are composed of långbanite. Analyses of these tablets, and of the columnar crystals, show that the general formula of the mineral is $R_2O_3 + RR'O_3$.

In a subsequent paper (*Geol. Fören. i Stockholm Förh.*, **13**, 271), H. Bäckström gives further analyses of this mineral, showing that it is an isomorphous mixture of compounds of the general formula $R^mR^nO_3$ (compare Abstr., 1891, 1436). B. H. B.

Mineral Chemical Studies. By S. J. THUGUTT (*Jahrb. f. Min.*, 1893, ii, Ref. 10—12).—The author has prepared and analysed alteration and substitution products of various minerals by the method successfully adopted by Lemberg, with a view to obtaining information on the constitution of these minerals. His experiments relate to the sodalite group, the formation of kaolin, the alterations of corundum, of diaspore, and of natural glasses, basic sulphates, and sulphoferrites. B. H. B.

Astochite. By H. SJÖGREN (*Jahrb. f. Min.*, 1893, ii, Ref. 37—38; from *Geol. Fören. i Stockholm Förh.*, **13**, 604).—Astochite, described by the author as a new member of the amphibole group, occurs in blue aggregates in association with rhodonite at the Långban mine, in Wermland. It crystallises in the monoclinic system, and the results of analysis proved it to be a metasilicate, in which the compounds $(Mg,Mn,Ca)SiO_3$ and $(Na,K,H)_2SiO_3$ occur. The latter silicate has not hitherto been met with in the hornblende series.

B. H. B.

Astochite and Dahllite. By A. HAMBERG (*Jahrb. f. Min.*, 1893, ii, Ref. 39—40; from *Geol. Fören. i Stockholm Förh.*, **13**, 801).—The author discusses the two alleged new minerals astochite and dahllite. Sjögren's astochite, he shows, is identical with the mineral richterite analysed by Michaelson and Igelström. The mineral described by Brögger and Bäckström as dahllite he regards as identical with staffelite, a mineral described by Stein, Streng, Petersen, and Sandberger. B. H. B.

Dioptase from the Congo. By A. LE CHATELIER (*Compt. rend.*, **116**, 894—896).—Some interesting specimens of dioptase have been found by the author at the Mindouli copper mines, on the road from Loango to Brazzaville. These mines are worked by the natives on a large scale. At the most important of the four centres of activity there are 150 to 200 shafts, and 300 to 350 natives employed in the extraction of malachite. The dioptase occurs in geodes, in quartzite, or in a crystalline rock, shown, on analysis, to consist of a mixture of quartz, willemite, and lead and calcium carbonates. Near the dioptase, an amorphous copper silicate is found, resembling chrysocolla, but in composition identical with dioptase. The deposit, which

appears to be the capping of a vein not yet discovered, is described in detail by the author, and analyses of the various minerals are given. B. H. B.

Composition of Helvine. By A. Kengott (*Jahrb. f. Min.*, 1893, ii, Mem. 72—74).—The formula deduced from published analyses, by Bäckström and by Rammelsberg, of helvine from Norway is $6(2RO,SiO_2) + MnS_2$, whilst that deduced from Teich's analysis of helvine from the Ural is $6(2RO,SiO_2) + 2MnS$. Analyses of danalite and of the Ural helvine lead to the latter formula, and it appears desirable that further analyses should be made of the Norwegian helvine, to ascertain whether this mineral also should have the same formula assigned to it. B. H. B.

The Formula of Tourmaline. By A. Kengott (*Jahrb. f. Min.*, 1893, ii, Mem. 71).—In a former paper (Abstr., 1892, 1415), the author showed, by the calculation of a number of analyses, that the whole tourmaline series might be regarded as mixtures, in varying proportions, of two isomorphous substances: A represented by the formula $3R_2O,SiO_2 + 5(R_2O_3,SiO_2)$, and B represented by the formula $2(3RO,SiO_2) + R_2O_3,SiO_2$. A recent analysis, by Katzer, of the tourmaline from Benitz, in Bohemia; affords a confirmation of this theory, the author's calculations showing that it consists of 2 parts of A and 1 of B. B. H. B.

Synthesis of Minerals. By J. Morozewicz (*Jahrb. f. Min.*, 1893, ii, Mem. 42—51).—The author gives further details of his experiments (this vol., ii, 19) on the synthesis of hauyn, and concludes that minerals of that group may be formed without difficulty from a silicate magma of corresponding composition, if the melting point of such magma is not too high. At high temperatures, these minerals cannot be formed, and, in their place, anorthite and nepheline are produced.

The author also gives the results of some experiments on the formation of quartz, biotite, and sanidine from molten liparite.

B. H. B.

Zeolites from Brazil. By E. Hussak (*Zeit. Kryst. Min.*, **21**, 405—408).—The author gives a lengthy description of the zeolites from the augite-porphyrite of S. Paulo and Santa Catharina. Heulandite, in fine, large crystals, gave, on analysis, the following results:—

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
58·10	16·67	5·90	3·26	0·61	16·16	100·70

Other analyses given are the following:—

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.
I.	47·61	26·80	7·08	7·80	12·11	101·40
II.	60·82	16·67	4·25	1·73	18·12	101·59
III.	45·96	26·03	13·53	—	13·67	99·19

I, Mesolite from the Serra de Botucatú; II, desmine from the Serra de Brotas; and III, scolezite from the Serra de Tubarão, in the State of Santa Catharina. B. H. B.

Meteoric Iron from Augustinovka (Russia). By S. MEUNIER (*Compt. rend.*, **116**, 1151—1153).—The meteorite from Augustinovka, Ekaterinoslav, weighs 25 lbs., and is remarkable because it was found in the post-tertiary clay. Examination of some of the partially oxidised external layers shows that the meteorite contains schreibersite, insoluble in hydrochloric acid, but soluble in nitric acid, together with some nickel and phosphoric acid, but mixed, in these altered and oxidised outer layers, with a large proportion of ferric oxide. C. H. B.

Physiological Chemistry.

Artificial and Natural Digestion. By R. H. CHITTENDEN and G. L. AMERMAN (*J. Physiol.*, **14**, 483—508).—Natural digestion is admittedly different from digestion carried out in a flask. It is probably more rapid and more complete, the products of digestion being continually removed and fresh juice poured out. This was well pointed out by S. Lea (Abstr., 1890, 536), who dealt especially with starch. He found that, by carrying out the digestion in a dialyser in constant movement, the intermediate dextrins were found in small amount only, and surmised that, in the body, the conversion into sugar was practically complete. In the present research, it is gastric juice that was the subject of study, and the method adopted was practically the same as in Lea's experiments. This method, although more like natural digestion than that carried out in a flask, is still imperfect, as it is impossible to imitate the vital selective action of the cells of the lining of the stomach and intestines.

It was found that the amount of true peptone, in comparison with albumose, was not markedly different in the dialyser and flask experiments, and the opinion is expressed that the normal action of gastric juice is not to completely peptonise proteïd, but rather to act as a preliminary to the more vigorous action of the pancreatic juice. This supposition was confirmed by examining the contents of the human stomach after a meal of egg-white. The amount discovered was small, and it is not easy to say exactly how the loss occurs; doubtless it is partly by absorption through the gastric walls, and partly by onward passage to the duodenum. The fact, however, that peptone and proteose were found an hour or more after the meal shows that absorption from the stomach is not immediate, as has often been taught. The proportion of proteose is always greater than that of peptone.

In the course of the experiments with dialysis, it was noticed that albumoses were discoverable in the dialysate. This was not unex-

pected. On testing this question quantitatively, it was found that the proteoses were diffusible to a considerable extent, but not nearly so much as peptone. A curious fact, which was unexpected, was that deutero-proteose is less diffusible than proto-proteose. Proto-gelatose is fairly diffusible, but it has a somewhat lower endosmotic equivalent than the corresponding proteose. Elevation of temperature increases the rate of osmosis, especially of the proteoses.

W. D. H.

Note by Abstractor.—The greater diffusibility of proto-proteose than that of deutero-proteose has also been noted by Kühne (Abstr., 1893, i, 234). W. D. H.

Physiology of the Embryonic Heart. By J. W. PICKERING (*J. Physiol.*, **14**, 383—466).—Experiments on the hearts of chick embryos, mostly 72 hours old, were performed by exposing the embryo by a hole in the egg shell, and keeping it *in situ* in a water-bath, the upper surface of which was covered by a glass plate. The heart of each embryo has an individual rhythm, which varies directly with the temperature. Extremes of temperature stop the heart in an expanded condition. Caffeïne, digitalin, and strophanthin modify the tone of the embryonic heart, and finally stop its ventricle in strong systole.

Strychnine, morphine, veratrine, nicotine, amylic nitrite, and potassium chloride stop the heart in an atonic condition. An antagonism exists between veratrine and potassium chloride, and between nicotine and potassium chloride, in their action on the embryonic heart. Morphine acetate and amylic nitrite in the final phases of their toxic action reverse the rhythm of the embryonic heart. Atropine has only a slight depressant action on the rhythm. Muscarine nitrate has apparently no specific action on the hearts of embryos between the 57th and 96th hours.

Chloroform depresses the heart to stoppage in extreme diastole. Ether primarily stimulates, and in large doses depresses it.

The fact that the heart at this period has no nerves, furnishes a means of distinguishing in the action of drugs those that act on the muscular from those that act on the nervous structures of the heart. W. D. H.

Proteïds of the Crystalline Lens. By C. T. MÖRNER (*Zeit. physiol. Chem.*, **18**, 61—106).—The crystalline lens of the eye yields a certain amount of proteïd matter to water and saline solutions. About 48 per cent. of proteïd remains undissolved. This insoluble substance is termed albumoïd, and is most abundant in the inner, denser portions of the lens. It yields no nucleïn on gastric digestion, and the small amount of phosphorus it contains is due to inorganic phosphates. The soluble proteïds of the lens are also not nucleïn compounds. About 2 to 4 per cent. of the soluble proteïd is albumin; the rest is globulin. The globulin is precipitated by saturation with magnesium sulphate, but not by sodium chloride; in this it resembles vitellin. The globulin consists of two proteïds, α-crystallin and β-crystallin.

α-Crystallin is completely precipitable by saturation at 30° with

magnesium sulphate or sodium sulphate; by the addition of $1\frac{1}{2}$ times its volume of saturated ammonium sulphate solution by a stream of carbonic anhydride, and by very dilute acetic or hydrochloric acids. It coagulates at 72°. It contains N, 16·68; S, 0·56; C, 52·83; and H, 6·94 per cent. $[\alpha]_D = -46·9°$.

β-Crystallin differs from this in its coagulation temperature (64°). $[\alpha]_D = -43°$. It contains 17·04 nitrogen and 1·27 sulphur per cent.

The proportion between these four proteïds is given in the following table:—

	Total proteïds.	Soluble proteïds.	In fresh lens.
Albumoïd	48·0 per cent.	—	17·0 per cent.
α-Crystallin	19·5 „	37 per cent.	6·8 „
β-Crystallin	32·0 „	62 „	11·0 „
Albumin	0·5 „	1 „	0·2 „
Total proteïds	—	—	35·0 „

α-Crystallin is more abundant in the outer, β-crystallin in the inner, portions of the lens; the albumin is equally distributed. The lens contains no keratin. W. D. H.

Proteïds of Spleen and Thyroid. By F. Gourlay (*Proc. Physiol. Soc.*, 1893, 8—9).—The proteïds obtainable from the spleen are precipitable from saline solutions by saturation with magnesium sulphate, and therefore fall into the globulin or nucleo-albumin class. The amount of albumin is small. They resemble very closely the proteïds described by Halliburton as obtainable from lymphoid structures. Further, the nucleo-albumin can be prepared either by the acetic acid method of Wooldridge or the sodium chloride method of Halliburton. It causes intravascular coagulation. Spleens were placed under alcohol for some months. The proteïds were entirely coagulated, and no trace of peptone or proteose was discoverable. The opinion is expressed that Schmidt's cytoglobin is nucleo-albumin which had escaped coagulation by insufficiently long exposure to alcohol.

The absence of proteoses and peptone is important in view of Martin's discovery that the albumoses of disease (diphtheria, tetanus, &c.) accumulate in the spleen. Devoto's modification of the ammonium sulphate method was also used with the same negative results. If the spleens are not perfectly fresh, proteoses are discoverable. They are probably formed *post mortem* by a process of self-digestion or putrefaction. v. Jaksch states that normal spleens do contain "peptone"; it is possible that he did not use the perfectly fresh organs.

The proteïds obtainable from the thyroid are very similar. The yield of nucleo-albumin by Wooldridge's method is, however, small; the aqueous extract is rendered cloudy by the addition of weak acetic acid, but there is little or no precipitation. The yield by the sodium chloride method is large. The question then arises, Is some of this derived from the colloïd substance? It appears that it is so, and the

method introduced by Lilienfeld and Monti (this vol., ii, 135) for the localisation of phosphorus led to positive results. The so-called colloïd substance is stained as darkly as, or in some cases more darkly than, the cells. The hypothesis that colloïd substance is not mucin is confirmed by the fact that after boiling thyroids with dilute sulphuric acid, there was no formation of a reducing sugar.

W. D. H.

Action of Physiological Saline Solution on Blood Corpuscles. By H. J. Hamburger (*Centralbl. f. Physiol.*, **7**, 161—165).—In recently published papers, Bleibtreu and others (this vol., ii, 331, 332) have brought forward a method of estimating the volume of the blood corpuscles by analysing mixtures of blood and physiological saline solution (0·6 per cent. sodium chloride solution), on the supposition that this reagent has no influence on the corpuscles.

In the present paper, it is pointed out that this supposition is not borne out by facts. The saline solution has a considerable influence on the volume of the corpuscles; in the ox and pig, the strength of the solution should be 0·9 per cent., which has the same water attracting power as the serum of those animals. But even this is not an indifferent fluid, for it dissolves out a good deal of proteïd from the corpuscles, although not so much as physiological salt solution does. The only completely indifferent fluid known is blood serum.

W. D. H.

Coagulation of Blood. By A. E. Wright (*J. Pathol. and Bacteriol.*, **1**, 434—450).—A critical account is given of the various theories of blood coagulation. None is absolutely satisfactory, nor applicable to all forms of blood or blood plasma obtained by artificial means. The importance of nucleo-albumin and calcium salts is recognised; the fibrin ferment theory, as taught by Schmidt and Hammarsten, is considered to have little or no substratum of fact.

With regard to the influence of carbonic anhydride, it is suggested that the loss of coagulability of peptone blood may be associated with the impoverishment of the blood in this gas. Peptone plasma is rich in dissolved nucleo-albumins; the white corpuscles having dissolved, or, at least, disappeared, the alkalinity of peptone plasma is reduced; this may be due to the solution of nucleo-albumin, a substance with acid properties, and further the loss of carbonic anhydride may be assumed to be due to the nucleo-albumin driving out the gas from its combination with bases. Peptone plasma gives a heavy precipitate of nucleo-albumin on adding a weak acid, probably because it is thereby dissociated from its combination with bases. This precipitation of nucleo-albumin would place it at the disposal of the plasma for purposes of coagulation.

If this explanation holds true, the coagulation of peptone plasma by carbonic anhydride would be a direct reversal of the driving out of the gas which results from peptone injection, and the phenomena of coagulation in peptone plasma are governed by the same conditions as those of intravascular coagulation after injection of Wooldridge's "tissue fibrinogen." The distribution of coagulation after such injections is determined by the amount of carbonic anhydride which is present in the various vascular areas.

W. D. H.

Iron in Chlorosis. By R. STOCKMAN (*Brit. Med. J.*, 1893, i, 881—885, 942—944).—It is an undoubted fact that iron administered in an inorganic form does good in cases of chlorosis. The present paper dwells on the fact that inorganic iron is the best remedy, the cure being quicker than when iron is given in organic compounds, such as blood or hæmatin; Kobert's (*St. Petersburg Med. Woch.*, 1891) preparations, hæmol and hæmogallol, prepared from blood, although tasteless and unirritating, did not give encouraging results.

The results of the present paper also tend in favour of the theory that iron is absorbed, and does not simply act as a stimulant, or by combining with hydrogen sulphide in the intestines, as Bunge considers. The grounds on which this conclusion is based are—

1. Iron inorganic compounds cure chlorosis when given hypodermically.

2. Sulphide of iron itself cures chlorosis.

3. Bismuth, manganese, and other drugs—which are just as capable as iron of combining with hydrogen sulphide—do not cure chlorosis.

Full details of cases are given.

Why inorganic iron does not increase the hæmoglobin of healthy people is an unsolved problem which is hardly touched in the present research. W. D. H.

Action of Drugs containing Iron. By C. T. MÖRNER (*Zeit. physiol. Chem.*, **18**, 13—20).—Many observers state that inorganic iron salts are not absorbed. The normal supply of iron is hæmatogen, an iron-containing organic compound of the nature of nucleo-albumin. If growing animals are deprived of this, they waste in spite of the administration of inorganic iron. Bunge explains the usefulness of inorganic iron in chlorosis by supposing that the putrefaction processes in the intestines destroy hæmatogen, but that this is protected by the presence of simple iron compounds which leave the body in the fæces as iron sulphide. In chlorosis, also, the normal antiseptic, the hydrochloric acid of the gastric juice, is less than normal. These views of Bunge suggest certain difficulties, and a question here investigated is, Are iron salts antiseptics? The amount of ethereal hydrogen sulphates in the urine is a measure of the amount of putrefactive change in the intestine. By experiments on the author's own person for five periods, two without and three with iron, the proportion of the two classes of urinary sulphates was practically the same (1 : 10·4 for the iron periods, 1 : 10·9 for the other periods). Iron salts are, therefore, not antiseptics; their usefulness rather depends on the readiness with which they form the sulphide and so remove hydrogen sulphide from the alimentary canal. W. D. H.

Physiological Action of Pentoses. By W. EBSTEIN (*Virchow's Archiv*, **132**, 368—369; compare Abstr., 1892, 1506).—M. Cremer *Sitz. Ges. Morphol. Physiol. München*, 1893, Heft 1) fed starving rabbits on pentoses and found that there was a small increase in the glycogen of their livers. This research on a herbivorous animal does not, however, touch the question formerly investigated by the author, which

was the action of pentoses on the human organism, and the correctness of his results is affirmed. W. D. H.

Abnormal Milk. By W. W. Cooke and J. L. Hills (*Exper. Stat. Record*, **4**, 487; from *Vermont Stat. Rep.*, 1891).—The milk was from a Jersey cow, and the last milking before she went dry. The following results were obtained:—

Total solids.	Fat.	Solids not fat.	Caseïn and albumin.	Ash.	Milk sugar.
28·43	14·67	13·76	9·98	1·44	2·33

The milk is remarkable for the small amount of milk sugar, the large amounts of proteïds and ash, and the very large amount of fat. There seems to be no other record of a milk analysis showing more fat than the solids not fat. N. H. M.

Fœtal Urine. By T. A. Helme (*Brit. Med. J.*, 1893, i, 1261—1262).—The presence of urea in the amniotic fluid has been generally attributed to fœtal urine, but no direct proof that fœtal urine contains urea has hitherto been forthcoming. In the present instance, a small quantity was accidentally obtained during delivery; and the following is the analysis made, comparative experiments being performed with the urine secreted shortly after birth.

The fœtal urine contained no sugar, albumin, phosphates, or sulphates. Urea (0·15 per cent.), creatinine, and chlorides were present. Eight hours after birth, sugar, albumin, and phosphates were absent, but sulphates, chlorides, creatinine (in larger amount), and urea (0·3 per cent.) were present. W. D. H.

β-Hydroxybutyric acid in the Organism. By T. Araki (*Zeit. physiol. Chem.*, **18**, 1—12).—The appearance of this acid in diabetic urine is not fully understood, but may be partially dependent on insufficient oxidation processes in the organism. The present paper does not, however, work out this aspect of the question, but relates to some of the properties of β-hydroxybutyric acid.

By distillation of an aqueous solution of the acid, a small quantity of crotonic acid is obtained. On subjecting it to putrefaction, crotonic acid, acetic, and probably other fatty acids are obtained, in addition to methane and carbonic anhydride. Administered to animals (rabbits, dogs, frogs), their urine gives the tests in many cases for acetone and acetoacetic acid if oxidation processes in the organism are diminished simultaneously by carbonic oxide poisoning. This result lends support to Minkowski's (*Arch. exp. Path. Pharm.*, **18**, 42) theory that these substances in diabetic urine originate from β-hydroxybutric acid. W. D. H.

Formation of Uric Acid. By G. Salomon (*Virchow's Archiv*, **132**, 370).—In relation to Horbaczewski's work on uric acid (Abstr., 1892, 646), the author advances a claim for priority. W. D. H.

Urobilin. By F. GRIMM (*Virchow's Archiv*, **132**, 246—289).—In the fasting condition, normal urine contains no urobilin. At the conclusion of gastric digestion, a larger or smaller quantity appears. Any great amount of the pigment is, however, a pathological condition, the most important cause being the circulation of unorganised blood pigment in the vessels, as after a hæmatoma. In nephritis, it also occurs.

A large number of cases illustrating the presence of urobilinuria in various diseases are given fully. W. D. H.

Mucin Granules of Myxine. By E. W. REID (*J. Physiol.*, **14**, 340—346).—The mucus of the hag fish (*Myxine glutinosa*) is secreted in the form of granules peculiar for their size (2 to 5 μ) and flattened oval shape. These granules are produced in mucous cells developed in the slime glands. A solution of the substance of which they are composed presents most of the features of a mucin, but differs from it in not yielding a reducing sugar after prolonged boiling with dilute sulphuric acid. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Nitrogen-fixing Micro-organisms. By BERTHELOT (*Compt. rend.*, **116**, 842—849).—Various nutritive matters, such as humic acid, Cohn's liquid, kaolin with humic acid, sugar, &c., were inoculated with soil organisms and the bacteria from leguminous roots, &c., and the gain of nitrogen, if any, determined. The experiments were conducted in flasks of 600 c.c. to 6 litres capacity.

I. *Experiments with Soil Organisms.*—The following experiments were made: (1) mixed soil bacteria in humic acid, in humic acid and kaolin, and in kaolin; (2) a bacillus isolated from soil in humic acid and in Cohn's liquid; (3) check experiment, not inoculated; (4, 5, and 6) three different soil bacilli, each in various nutritive media. The results showed a considerable gain of nitrogen where the mixed bacteria were employed, and also in experiments 2 and 5, whilst in the check experiment and in Nos. 4 and 6 there was practically no gain of nitrogen.

II. *Experiments with Leguminous Root Bacteria.*—The bacteria were obtained from lupin roots which had nodules. The two experiments lasted about four months, and each showed a gain of 50 per cent. of the initial nitrogen.

III. *Experiments with Aspergillus niger.*—The experiments made with pure cultures of *Aspergillus niger* showed a gain of 18—37 per cent. nitrogen; a check experiment with Cohn's liquid and tartaric acid, not seeded, showed no sign of nitrogen. It was noticed that the tartaric acid employed was largely consumed or destroyed under the influence of *Aspergillus niger*.

IV. *Experiments with Alternaria tenuis.*—The cultivations were pure and developed well. The nitrogen fixed amounted to 36, 49, 50, and 98 per cent. respectively of the initial amounts.

There are, therefore, non-chlorophyllous micro-organisms of very different character which have the power of fixing nitrogen. These organisms do not seem to be able to be sustained by the carbon and hydrogen resulting from the decomposition of carbonic anhydride and water, but require organic carbon and hydrogen in such a form as sugar and tartaric acid, &c. It seems also necessary that nitrogen should be present in the nutritive matter in order to give the minimum vitality indispensable for the fixation of free nitrogen. On the other hand, when the amount of combined nitrogen present becomes large, the organisms prefer to utilise it rather than to fix free nitrogen, and will develop more luxuriantly than when they have to depend on uncombined nitrogen. It is this that limits the fixation of elementary nitrogen in soils (compare *Ann. Chim. Phys.* [6], **14**, 487).

The carbonaceous matter of soils would disappear more or less quickly if not regenerated by chlorophyllous plants. The agents which bring about nitrogen fixation and carbon fixation may live independently of each other or may be associated by symbiosis, as in the case of the Leguminosæ. In any case, the fixation of nitrogen does not take place in the higher plants, but in certain lower micro-organisms present in soil. N. H. M.

Pentosans in Plants. By G. DE CHALMOT (*Amer. Chem. J.*, **15**, 276—285).—Pentosans decrease in the seeds of peas and corn (*Zea Maïs*, L.) during the germination, but appear again in the roots and stems; they are therefore transferred. The total amount of pentosans, however, increases during the germination. The amount of cellulose pentosans also increases, but in the case of peas the difference is only very slight. G. T. M.

Products of Cassava. By E. E. EWELL and H. W. WILEY (*Amer. Chem. J.*, **15**, 285—289).—The authors have extended their work, an account of which was published four years ago (Wiley, *Agric. Science*, **2**, No. 10, pp. 256, *et seq.*). They find that the root of *Jatropha manihot* or Aipi contains very little mineral matter, 0·5 per cent. in the fresh root, and that the plant is, therefore, one which seems particularly well suited to feed almost exclusively from the air and water. As it requires the minimum of fertilisation, it can be recommended for sandy soils. G. T. M.

Amount of Starch in different Varieties of Potatoes. By A. PETERMANN (*Bied. Centr.*, **22**, 263—266; from *Bull. Stat. Agron. Gembloux*, 1892, No. 51).—The average minimum and maximum percentages of starch found in a large number of different kinds of potatoes examined in 1889, 1890, and 1891, were as follows:—

	1889.	1890.	1891.
Maximum.....	9·8	9·4	11·1
Minimum.....	24·0	26·1	23·3
Average	15·2	16·5	16·6

A table is given, showing the amount of starch, the power of resistance to disease, and the properties of 50 varieties of potatoes. The results of the investigation show that it is possible to produce potatoes which give large crops and at the same time contain a high percentage of starch. N. H. M.

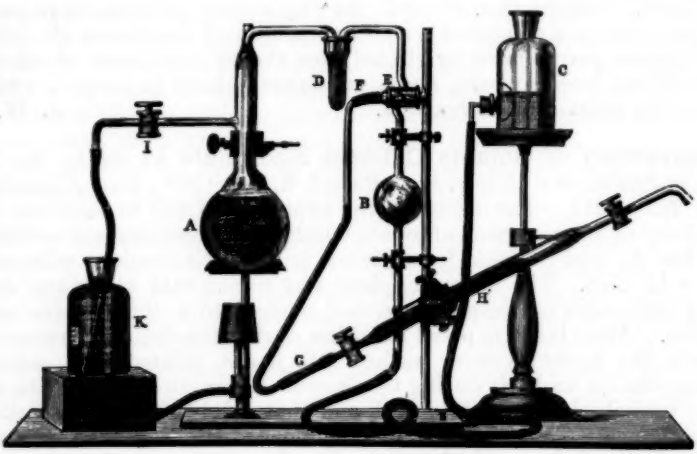
Reserve Proteïd of the Asparagus Root. By S. H. Vines and J. R. Green (*Proc. Roy. Soc.*, **52**, 130—132).—The watery extract of asparagus root contains a proteïd which is slightly precipitated from solution by sodium chloride, and completely by ammonium sulphate. Besides this, which is the only proteïd present, there exist in the solution a substance which is precipitated by sodium chloride, a substance precipitated by alcohol from the solution from which the proteïd has been removed, and a substance soluble in alcohol, which gives the xanthoproteïc reaction. J. W.

Reversion of Soluble Calcium Phosphate in Soil. By M. Stahl-Schroeder (*Exper. Stat. Record*, **4**, 587—589; from *J. Landw.*, **40**, 213—221).—The object of the experiments was to ascertain the rapidity of the reversion of superphosphate, in concentrated solution, to the di- and tri-basic forms, when mixed with chalk or with soils poor in lime. The superphosphate was mixed with chalk and with clay and arable soil respectively, and made into a thick paste with water. After being exposed in dishes during the desired number of hours, the mixtures were washed into flasks, diluted to a definite bulk, shaken, and left during two hours. A portion was then filtered, and the soluble phosphoric acid, and that soluble in citrate solution, determined. When chalk was employed, the reversion was extremely rapid, but with the two soils only a little more than half the phosphoric acid became insoluble in 20 days. The results indicate that with liberal applications of superphosphate on sandy soils poor in lime, a part of the phosphoric acid may be lost in drainage. Clay soils are likely to lose less. In sandy soils, the application of precipitated phosphate of lime, basic slag, or phosphorite meal is recommended. Composting of the latter with peat and potassium sulphate would be very advantageous, inasmuch as the potassium salts in conjunction with the vegetable acids of the peat would gradually render the phosphoric acid available, and, at the same time, the vegetable matter would improve the water-holding capacity of the soil.

N. H. M.

Analytical Chemistry.

Apparatus for extracting the Gases dissolved in Water. By G. J. W. Bremer (*Rec. Trav. Chim.*, **11**, 278—283).—A is a flask of about 600 c.c. capacity, which contains the water to be examined, EBC is a mercury pump, and FGH the tube in which the gases are collected. The pump is worked by alternately lowering and raising the mercury reservoir C, the stopcock E being so manipulated that the air, or, in the actual experiment, the gases to be examined, is first aspirated into B (capacity 135 c.c.), and then driven out through F. The joint D, connecting the pump with A, consists of a short



tube with an indiarubber cork, through which the two tubes pass; some mercury is placed over the cork to ensure that the joint is air-tight. In the experiment, A is partially exhausted, either with an ordinary pump, or by placing some water in it, and boiling, so that the steam drives out the air through I, the stopcock E being closed. Water is then suffered to rise in the tube as far as I, and the vacuum is completed by means of the pump EBC. The vessel K (about 500 c.c. capacity) is now completely filled with the water to be examined; by opening the stopcock I, this water is admitted into A in successive portions; after each addition, the water in A is boiled, and the gases evolved are aspirated into FGH by means of the pump. K is not quite emptied, and the amount of water actually used in the experiment is determined by finding how much water is required to refill K. The experiment occupies half-an-hour. C. F. B.

Bottle for taking Samples of Water at known Depths. By G. J. W. Bremer (*Rec. Trav. Chim.*, **11**, 284—285).—The bottle

stands in a zinc tray, which is weighted with lead, and joined by copper wires to a ring round the neck of the bottle; to this ring is attached the string used for lowering the whole. The bottle is provided with an indiarubber cork, through which pass two tubes, one ending just under the cork, the other reaching to the bottom of the bottle. The upper ends of these tubes project somewhat above the cork, and are slightly enlarged; they are plugged by inserting into them the two ends of a short piece of indiarubber tubing, into which ends short pieces of glass-rod have been pushed. To the top of the indiarubber loop thus formed a string is attached; this is pulled when the bottle has reached the desired depth, the plugs are thus removed from the two tubes, and the water enters the bottle by the longer of the tubes, the air escaping by the other. C. F. B.

Sjöqvist's Method of estimating the Free Hydrochloric Acid in Gastric Juice. By S. Bondzyński (*Zeit. anal. Chem.*, **32**, 296—302).—The method consists in evaporating gastric juice with excess of barium carbonate, incinerating the residue and determining the barium which has become soluble in the form of chloride. Barium chloride bears, without noteworthy decomposition, ignition at a higher temperature and for a longer time than are required for the incineration, but when mixed with organic substances containing phosphorus and sulphur, a portion of the barium is rendered insoluble in the form of phosphate and sulphate. The addition of barium acetate obviates this source of error, and the estimation may be made in the following manner:—1 gram of barium carbonate is dissolved in acetic acid in a platinum basin, and the solution evaporated to dryness; 25 c.c. of the filtered gastric juice, together with more barium carbonate, are added, the mixture is dried and incinerated to a grey ash. The soluble matters are filtered, and, after adding 25 c.c. of N/10 sodium carbonate, are made up to 125 c.c. The excess of soda in 100 c.c. is then titrated. Then, a being the number of c.c. of soda found, $(20 - a)5$ gives the amount of free hydrochloric acid in 100 c.c. of the gastric juice, expressed in c.c. of N/10 acid.

M. J. S.

A Source of Error in the Volumetric Estimation of Chlorides by Mohr's Method. By W. G. Young (*Analyst*, **18**, 125—129).—The author has found that when estimating chlorine in samples of water without previous concentration, the results obtained are considerably in excess, and they are worse still if the temperature during titration is somewhat high. This is caused by the slight solubility of silver chromate, which requires for every 6 parts 100,000 parts of water at 15·5°, and only one-third of this amount at 100°.

In estimating small quantities of chlorides, it is therefore advisable to evaporate almost to dryness before titration, and to prevent over-dilution, the standard silver should not be too weak.

L. de K.

Estimation of Sulphur in Organic Liquids. By R. Höland (*Chem. Zeit.*, **17**, 99—100; 130—131).—The accurate estimation of small quantities of sulphur in substances such as tar oils, &c., is still a matter of some difficulty. The author has, however, obtained satis-

factory results by burning the sample in a combustion tube with a mixture of 5 parts of barium carbonate and 1 part of potassium chlorate. The details are practically those of an ordinary combustion, the substance being, however, not inclosed in glass bulbs, but dropped straight on to the back part of the mixture from a 3 c.c. weighed pipette.

The contents of the tube are afterwards digested in dilute hydrochloric acid, and any barium sulphate is then collected and weighed.

L. DE K.

Estimation of Nitrogen in Nitrates. By T. F. SCHMITT (*Chem. Zeit.*, **17**, 173).—The author has slightly modified his process. 10 grams of the sample is dissolved in 500 c.c. of water. 10 c.c. of glacial acetic acid and 10 grams of a mixture of equal parts of iron and zinc powder are put into a 750 c.c. round-bottomed flask, and 25 c.c. of the nitrate solution added from a slow-running pipette. After 10 minutes, when no more gas is evolved, 200 c.c. of water and 30 c.c. of aqueous soda (sp. gr. 1·25) are added and the ammonia is distilled off as usual.

To estimate the total nitrogen in nitrated manures, the author first reduces the substance with the acetic acid mixture, and then boils with excess of sulphuric acid in order also to convert the nitrogenous matter into ammonia.

L. DE K.

Estimation of Phosphoric acid. By A. VILLIERS and F. BORG (*Compt. rend.*, **116**, 989—993).—In the complete absence of iron, aluminium, silica, and reducing agents, phosphorus can be accurately estimated in the following manner. The liquid is mixed with about 100 c.c. of the reagent (prepared by dissolving 150 grams of ammonium molybdate in 1 litre of water and pouring this solution into an equal volume of nitric acid of sp. gr. 1·2) for every 0·1 gram of phosphoric acid present. In order to obtain a precipitate that settles rapidly, the reagent should be poured down the sides of the vessel containing the cold solution, and the liquid should not be agitated until after two hours. Potassium compounds and other salts retard the formation of the precipitate, but after heating for four hours at about 40° precipitation is complete. The temperature of 40° should not be exceeded, and digestion should not be prolonged beyond four hours, otherwise the product will be impure. The precipitate is washed with water containing 20 per cent. by volume of the reagent, is collected on a dried and weighed filter, and dried at 100° for six hours. Thus obtained it has always the composition

$$P_2O_5,24MoO_3,3(NH_4)_2O,3H_2O,$$

and 1 part contains 0·03728 part of phosphoric anhydride, P_2O_5.

In presence of aluminium and iron, the precipitate contains a notable proportion of these metals, which also find their way into the ammonium magnesium phosphate produced from it in the usual way. The following plan, however, leads to exact results:—The precipitate is dissolved in ammonia, mixed with tartaric acid, made slightly alkaline with ammonia, and precipitated with magnesia mixture. The iron and aluminium remain in solution.

C. H. B.

Estimation of Boron. By H. Moissan (*Compt. rend.*, **116**, 1087—1091).—The boron compound is first converted into boric acid or a borate by the action of nitric acid, and then into methylic borate by distillation with methyl alcohol, as in Gooch's method. The apparatus consists of a small flask with a long neck, provided with a side tube and fitted with a glass stopper carrying a funnel with a stopcock. The side tube is connected with a vertical serpentine condenser, the lower end of which passes into a conical flask through a cork that also carries an exit tube to which is attached a set of bulbs containing dilute ammonia, in order to retain the whole of the methylic borate. A calcium chloride bath, heated by a Bunsen burner, is so arranged that it can readily be applied or removed from the distilling flask.

The substance is placed in the distilling flask, mixed with 1 c.c. of concentrated nitric acid, and distilled to dryness. It is then mixed with 10 c.c. of methyl alcohol, attached to the condensing apparatus, and again distilled. The operation is repeated four times, care being taken to distil to dryness every time before adding a fresh quantity of alcohol. 1 c.c. of water and 1 c.c. of nitric acid are then introduced into the apparatus, distilled as before, and the residue subjected to three more distillations with alcohol. In order to ascertain if all the boron has been expelled, a drop of the alcohol from the end of the condenser is ignited. If there is any green tinge in the flame, the residue in the flask must be again treated with nitric acid and again distilled with methyl alcohol.

A quantity of calcium oxide is strongly heated in a platinum crucible and weighed. The lime is carefully slaked and the distillate is added, taking care to avoid rise of temperature, and allowed to remain for 15 minutes. After ascertaining that the calcium oxide is in excess, the liquid is evaporated at a temperature below the boiling point of methyl alcohol, and the residue is strongly heated and again weighed. The increase in weight gives the quantity of boric anhydride.

The calcium oxide is most conveniently prepared by heating calcium nitrate in such a manner as to form a basic nitrate, which is easy to keep and which is converted into oxide by strongly heating when required.

The results obtained by this method are usually a little low; in the examples given the error varies from −0·27 to −0·4 per cent. of the boric anhydride present. C. H. B.

Estimation of Silicon in Pig Iron. By H. Rubricius (*Chem. Zeit.*, **17**, 101).—The author recommends the following simple process:—5 grams of the finely-divided sample is dissolved in 25—30 c.c. of hydrochloric acid (sp. gr. 1·15) with the aid of a gentle heat. When the metal has dissolved, the solution is diluted to about 150—200 c.c. and filtered. The insoluble matter is washed first with hot water, then with dilute hydrochloric acid (1 : 2), and then again with hot water. The filter, after drying, is put into a platinum crucible and heated until the paper is charred. The crucible is now ignited over the blowpipe, nitre being from time to time added until the carbon

has completely disappeared. 30 grams of ammonium chloride, which must be completely soluble, is now put into a large porcelain basin and dissolved in 75 c.c. of boiling water. The platinum crucible, with its lid, is put into this solution and the whole is boiled for some time. The action of the ammonium chloride on the alkali silicate causes the rapid and complete separation of hydrated silicic acid, which is collected on a filter and washed first with a dilute solution of ammonium chloride and then with boiling water. It is then ignited and weighed.

The test analyses are satisfactory. L. DE K.

Estimation of Potassium by the Lindo-Gladding Process. By T. BREYER and H. SCHWEITZER (*Chem. Zeit.*, **17**, 101—102).—The authors, in reply to Holleman (compare this vol., ii, 344), state that this process has also been investigated by Herff. The results, communicated to the American Association of Official Agricultural Chemists, fully confirm those previously obtained by the authors; not only do they not agree among themselves, but they are, as a rule, from 0·5 to 1 per cent. higher than those obtained by the Stassfurt method. The authors once more recommend that the Lindo-Gladding process should be abandoned. L. DE K.

Estimation of Alkalis in Silicates. By A. H. LOW (*Chem. News*, **67**, 185).—The following scheme is suggested for estimating alkalis in silicates:—1 gram of the finely powdered silicate is decomposed by warming gently with pure, strong hydrofluoric acid and a little sulphuric acid; it is then evaporated to dryness, cooled, mixed with a little aqueous ammonia, boiled, filtered, and washed with a little hot water. The filtrate is rendered strongly acid with hydrochloric acid, the least possible excess of barium chloride added, and the whole boiled and filtered, washing with hot water. This filtrate is then evaporated and gently ignited to expel ammonium salts, and, when cool, treated with ammonium carbonate and aqueous ammonia, boiled, and filtered, washing with hot water. The filtrate is evaporated to dryness in a tared platinum dish and weighed; this gives the mixed chlorides, which are separated in the usual manner. D. A. L.

Separation of Barium, Strontium, and Calcium. By R. FRESENIUS (*Zeit. anal. Chem.*, **32**, 312—317).—The following qualitative method permits the detection of small amounts of any one of the alkaline earths in presence of large quantities of the others. The carbonates are converted into nitrates and thoroughly dried at 180°, and, as soon as cold, triturated with equal volumes of absolute alcohol and ether, any residue being washed with the same mixture. Traces of strontium may pass into solution with the calcium, whilst traces of calcium may remain in the residue. To the solution, 2 drops of dilute sulphuric acid is added. Any considerable precipitate is undoubtedly calcium sulphate. A trifling precipitate may be due to strontium. In this case, 4 c.c. of water is added, and the ether-alcohol evaporated off. A few drops of ammonia are added, with 1 gram of ammonium sulphate, and the liquid is boiled and filtered, acidified

with acetic acid, and tested for calcium by ammonium oxalate. The nitrates insoluble in ether-alcohol are dissolved in 100 c.c. of water, acidified with 3 or 4 drops of acetic acid, heated to boiling, and treated gradually with potassium chromate until the solution is yellow and no longer gives an odour of acetic acid on boiling. After an hour, the barium chromate is filtered off, and a portion of the filtrate tested with ammonia and ammonium carbonate. If a bulky precipitate is produced, it must be strontium carbonate. If otherwise, the rest of the filtrate, mixed with a drop of nitric acid, is concentrated and precipitated with ammonium carbonate, any trifling precipitate is washed, converted into chloride, dried, dissolved in a mixture of 3 vols. of water and 1 vol. of alcohol, and boiled after adding 1 drop of potassium chromate. Strontium is indicated by a pulverulent, yellow precipitate.

For quantitative purposes, either the calcium may first be separated by treating the nitrates with ether-alcohol, and then the barium be separated from the strontium by potassium chromate, or the barium may first be separated as chromate, the calcium and strontium be precipitated as carbonates, converted into nitrates, and separated by ether-alcohol (Abstr., 1891, 110; this vol., ii, 301). Both methods give equally accurate results; the barium and calcium precipitates are pure, the strontium alone retaining a trace of calcium. M. J. S.

Quantitative Separation of the Metals of the Hydrogen Sulphide Group by means of Bromine Vapour. By P. Jannasch and W. Remmler (*Ber.*, **26**, 1422—1425; compare Abstr., 1892, 384, 540, 754).—Lead may be separated from tin (and from antimony) by treating the mixed sulphides as described in Abstr., 1892, 384; tin bromide volatilises, whilst lead bromide remains behind. The latter is converted into chloride by treatment with chlorine water, and then into sulphate, in which form it is weighed; the tin is converted into the oxide by repeated evaporation with nitric acid, and so weighed. Results good.

An attempt was made to improve the method by avoiding the precipitation with hydrogen sulphide. This was accomplished by mixing the material to be analysed with 6 to 10 times its weight of sulphur, and heating the mixture in a stream of dry hydrogen sulphide in a glass vessel shaped somewhat like a Liebig's drying tube; the metals remained behind as sulphides, and the excess of sulphur volatilised. The sulphides were then treated, in the same vessel, with bromine vapour as before described; good results were in general obtained. But it was found that metallic tin and tin oxide are only partially converted into sulphide by the above treatment, and the method consequently fails; if, however, 10 to 15 per cent. of iodine is added to the sulphur used, the tin is readily and completely converted into sulphide, and excellent analytical results are obtained. C. F. B.

Estimation of Lead. By A. H. Low (*Chem. News*, **67**, 178—179).—1 gram of ore is heated carefully with 10 c.c. of a mixture of equal parts of nitric acid and water until pretty well decomposed;

the nitric acid is then expelled by boiling with 10 c.c. of concentrated sulphuric acid, and, when cool, 10 c.c. of pure dilute sulphuric acid (1 : 9) and about 2 grams of Rochelle salt are added. When the latter is dissolved, 40 c.c. of distilled water is added, the whole boiled, the precipitate collected, washed with dilute sulphuric acid, and then heated with a saturated solution of ammonium chloride until all the lead sulphate is dissolved; the liquid is then filtered. Strips of pure aluminium are placed in the filtrate, which is boiled until the lead is all precipitated, cold water is added, the lead adhering to the aluminium removed, all the lead collected in a porcelain dish, washed with water, and finally with alcohol, then dried and weighed. A deduction of 3 per cent. is a fair allowance for arriving at the fire assay of a pure ore of the same grade. D. A. L.

Detection of Mercury in Urine. By S. Bondzyński (*Zeit. anal. Chem.*, **32**, 302—303).—In Ludwig's method, the mercury is precipitated from the urine by zinc powder, and then volatilised in a glass tube. Commercial zinc powder, however, contains cadmium, from which it cannot be freed completely even by prolonged and intense ignition in a stream of hydrogen. Nevertheless, even after ignition, it will, when only moderately heated in a tube, give off enough cadmium to form a mirror closely resembling mercury in appearance. Confirmation by means of iodine should, therefore, never be omitted; but it is safer to abandon the use of zinc, and to employ copper, in the form of powder, foil, or turnings.

M. J. S.

Estimation of Manganese in Ores. By A. H. Low (*Chem. News*, **67**, 162).—0·5 gram of ore is decomposed with 5 to 10 c.c. of hydrochloric acid or *aqua regia*, and most of the excess of acid is boiled off; the rest, after diluting the solution with 75 c.c. of hot water, is neutralised by boiling with excess of zinc oxide. A saturated solution of bromine is then added in excess, the superfluous bromine being expelled by heating; an excess of zinc oxide should, however, still remain. The precipitate is collected, washed with hot water, treated in a flask with 50 c.c. of dilute sulphuric acid (1 : 9), and dissolved by heating with excess of a standardised solution of oxalic acid, containing about 11·46 grams of acid per litre, and of which 1 c.c. corresponds with about 1 per cent. of manganese; after diluting with hot water, the excess of oxalic acid is titrated with standardised, approximately N/10 potassium permanganate. The amount of oxalic acid consumed by the manganic oxide is thus ascertained, and from it the percentage of manganese is readily calculated. The oxalic acid may be replaced by other reducing agents. D. A. L.

The Thiocyanate Test for Iron. By H. Schulze (*Chem. Zeit.*, **17**, 2).—The author has noticed that dilute solutions of ferric salts, containing no excess of mineral acids, fail, after some time, to give the characteristic red colour with a thiocyanate. The same happens with concentrated solutions on boiling. The probable cause of this is the conversion of the iron into Graham's soluble ferric hydroxide.

On addition of hydrochloric acid, the normal iron salt will be restored, and the test will be successful. L. DE K.

Estimation of Iron by an Iodometric Method. By E. NIHOUL (*Chem. News*, **67**, 196—198).—Ferric salts or ores containing iron in a ferric state are placed in a distillation flask provided with a tubulated stopper carrying a tube bifurcated above; the salt or ore is dissolved in hydrochloric acid by the aid of heat and the use of gaseous hydrogen chloride if required; a current of carbonic anhydride is then passed and continued throughout the operation; when all the air has been replaced, a slight excess of a strong solution of potassium iodide is introduced through the tube, and the contents of the flask are boiled; when most of the iodine has volatilised, gaseous hydrogen chloride is passed in; this not only ensures the volatilisation of all the iodine, owing to the decomposition of any potassium iodide which would otherwise hold some iodine back, but also the hydriodic acid formed aids the solution of ores, and, in fact, in some cases the potassium iodide may be added partly or wholly at the commencement of the operation, or a mixture of hydriodic and hydrochloric acids may be used in the first instance, taking care, of course, that all the air has been expelled. The distillate is received in a Volhard condenser, containing a solution of potassium iodide, and the iodine is estimated by sodium thiosulphate. Ferrous salts are oxidised in the flask before connecting up the condenser. Any free iodine in the hydriodic acid must, of course, be got rid of before using this acid for the purpose indicated. D. A. L.

Detection and Estimation of Formaldehyde. By A. TRILLAT (*Compt. rend.*, **116**, 891—894).—The liquid to be tested is mixed with a small quantity of dimethylaniline, acidified with sulphuric acid, and agitated briskly. It is then heated on a water-bath for half an hour. The product is made alkaline with sodium hydroxide, boiled until all odour of dimethylaniline disappears, and filtered. The filter-paper is then spread out on a porcelain dish, moistened with acetic acid, and some fragments of finely-powdered lead peroxide scattered upon it. In presence of formaldehyde, a deep-blue coloration appears, due to the formation of the hydrol of tetramethyldiamidodiphenylmethane.

When the solution to be tested is mixed with an equal volume of a neutral solution of 3 grams of aniline in a litre of water, a white cloud, due to the formation of anhydroformaldehydeaniline, appears after several hours. This reaction will detect 1 part in 20,000, but it is also given by acetaldehyde.

The detection of formaldehyde in foods, &c., is often impossible on account of the formation of compounds with various organic substances present in the food.

Formaldehyde can be estimated by weighing it as anhydroformaldehydeaniline, but the results, although strictly comparable amongst themselves, are not absolutely accurate.

Another method is based on the conversion of formaldehyde into hexamethyleneamine by the action of ammonia. The acidity of the solution is first determined by means of sodium hydroxide solution

and phenolphthalein; 10 c.c. is diluted with water and mixed with a measured excess of ammonia solution of known strength. A current of steam is then passed into the liquid, and the expelled ammonia is collected and estimated by means of standard acid. The difference between the quantity volatilised and the quantity originally added is the amount required to convert the formaldehyde into hexamethyleneamine. A little of the latter is volatilised in the process. C. H. B.

Estimation of Salicylic acid in presence of Phenols. By A. FAJANS (*Chem. Zeit.*, **17**, 69).—The colorimetric estimation of salicylic acid by means of ferric chloride cannot be carried out in aqueous solutions in the presence of phenols, but advantage may be taken of the fact that the latter give no coloration with ferric chloride in alcoholic solution. To estimate salicylic acid, the suspected liquid is acidified and extracted with ether, which is then allowed to evaporate. The residue is dissolved in 25—30 c.c. of absolute alcohol, introduced into a graduated tube, and mixed with a few drops of a 5 per cent. alcoholic solution of ferric chloride until the colour does not get any darker. In a similar tube, the same amount of an alcoholic solution of salicylic acid (2 : 10,000) is introduced, and then a sufficiency of ferric chloride solution. Finally, the darker of the two mixtures is diluted with absolute alcohol until they both show the same intensity of colour; the difference in volume is noticed, and the amount of salicylic acid is found by a simple calculation. Even in a mixture of 800 parts of phenol and 1 part of salicylic acid, the latter may be estimated with great accuracy. L. DE K.

Detection and Approximate Estimation of Cotton-seed Oil in Lard and Olive Oil. By F. GANTTER (*Zeit. anal. Chem.*, **32**, 303—308).—The author has obtained specimens of cotton oil, as well as of adulterated lard, which give no reaction with Becchi's silver nitrate test; this test can therefore no longer be depended on for the detection of this adulterant. The iodine absorptions of lard and cotton oil, 23—27 per cent. and 43—45 per cent. respectively, as determined by the author's process (this vol., ii, 309), differ widely enough to allow of the calculation, within 10 per cent., of the proportion of cotton oil present. To detect smaller amounts than 10 per cent., 1 c.c. of the perfectly dry, melted fat or oil is dissolved in 10 c.c. of light petroleum in a test tube, a single drop of concentrated sulphuric acid is added, and the whole well shaken. Pure lard gives only a straw-yellow to feeble reddish-yellow coloured liquid, from which, on repose, dark reddish-yellow drops slowly settle out, leaving a nearly or perfectly colourless upper liquor. Olive oil acquires a rather darker colour at first, but behaves like lard on standing. In presence of cotton oil, a deep brown to black colour is immediately produced, and remains unchanged even on standing for a long time. As little as 1 per cent. can thus be detected.

M. J. S.

General and Physical Chemistry.

Influence of Frictional Electricity on the Formation of Amalgams. By G. STAATS (*Ber.*, **26**, 1796—1797).—If plates of silver in contact with mercury be subjected to the discharge from an electrical machine, the quantity of amalgam produced in a given time is increased threefold. H. G. C.

Electrolysis of Alkali Salts. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **11**, 805—828).—The author has made experiments which show that when the aqueous solution of an alkali salt is electrolysed with a mercury cathode, a considerable time elapses from the beginning of the electrolysis before hydrogen makes its appearance. This observation proves that hydrogen is not a primary product of the electrolysis, but results from the action of the water of the solution on the alkali amalgam primarily formed by the discharge of the positive ion (the alkali metal). The time necessary for the appearance of the first bubble of hydrogen increases very slowly with diminution of the current strength, and (with a constant current of 0·05 amp.) increases with increase of concentration and lowering of temperature. It is practically constant for equivalent solutions of electrolytes with the same positive ion, but much larger for potassium salts than for lithium and sodium salts.

A theoretical investigation of this phenomenon shows that the electromotive force necessary for electrolysis increases at the beginning with the quantity of electrolytic products already separated. In general, however, secondary reactions occur, which prevent the continued accumulation of these products if the primary process goes on very slowly: in this case the electromotive force necessary for electrolysis is almost exclusively conditioned by these secondary reactions. If the result of the secondary processes is the same as it is in the case of alkali salts, then the E.M.F. necessary for the decomposition will also be the same, or nearly so. This conclusion is in accordance with the experiments of Le Blanc (*Zeit. physikal. Chem.*, **8**, 314), which therefore do not necessitate the assumption of a primary decomposition of the water.

From the observation of Shields (this vol., ii, 449) that a decinormal solution of sodium acetate is hydrolysed to the extent of 0·008 per cent., the electrical conductivity of pure water at 25° is calculated to be $0·56 \times 10^{-11}$, and this conductivity is greatly diminished when electrolytes are present. A salt of a strong acid and a strong base is hydrolysed to the extent of $1·21 \times 10^{-4}$ per cent. in decinormal solution, the absolute quantity of the hydrolysed part being almost independent of the concentration.

From the value for the electrolytic dissociation of pure water, it is possible to calculate the E.M.F. which must be used to develop from water, hydrogen and hydroxyl ions in a liquid already containing as many of these as are in normal solutions of strong acids or bases

The calculated value is 0·81 volt, whilst the experimental value of Le Blanc is 0·76 volt. J. W.

Magnetic Rotation of Liquids and Salt Solutions. By O. Schönrock (*Zeit. physikal. Chem.*, **11**, 753—786).—The author has determined the magnetic rotation of the compounds used by Landolt and Jahn in their investigation of dielectric constants (*Berlin Sitz-Ber.*, 21st July, 1892). The measurements were made at temperatures ranging from 20° to 30° with the following results.

		Specific rotation.	Molecular rotation.
Water	H_2O	1·000	1·000
Pentane	C_5H_{12}	1·45	5·81
Hexane	C_6H_{14}	1·39	6·66
Octane	C_8H_{18}	1·38	8·72
Decane	$C_{10}H_{22}$	1·39	10·99
Amylene	C_5H_{10}	1·59	6·18
Hexylene	C_6H_{12}	1·60	7·45
Octylene	C_8H_{16}	1·51	9·41
Decylene	$C_{10}H_{20}$	1·45	11·25
Benzene	C_6H_6	2·59	11·23
Toluene	C_7H_8	2·35	12·03
Ethylbenzene	C_8H_{10}	2·26	13·33
Orthoxylene	,,	2·26	13·31
Metaxylene	,,	2·16	12·73
Paraxylene	,,	2·17	12·79
Propylbenzene	C_9H_{12}	2·16	14·40
Isopropylbenzene	,,	2·17	14·44
Mesitylene	,,	1·94	12·92
Pseudocumene	,,	2·06	13·77
Isobutylbenzene	$C_{10}H_{14}$	2·09	15·53
Cymene	,,	2·00	14·89
Methyl alcohol	CH_4O	0·913	1·62
Ethyl alcohol	C_2H_6O	1·07	2·73
Propyl alcohol	C_3H_8O	1·13	3·76
Isopropyl alcohol	,,	1·19	3·97
Isobutyl alcohol	$C_4H_{10}O$	1·17	4·83
Amyl alcohol	$C_5H_{12}O$	1·20	5·89
Ethylenic chloride	$C_2H_4Cl_2$	1·004	5·52
Ethylidenic chloride	,,	0·976	5·36
Pyridine	C_5H_5N	2·01	8·82
Acetone	C_3H_6O	1·08	3·48
Diethyl ketone	$C_5H_{10}O$	1·14	5·43
Amyl ether	$C_{10}H_{22}O$	1·27	11·18

In order to investigate the influence of electrolytic dissociation on the rotation, the author measured the constants of various salts dissolved in water and other solvents. As most of the experiments

were made with mercury salts, which are very little dissociated even in aqueous solution, his results are inconclusive. Calcium chloride dissolved in water (12 per cent. solution) has a molecular rotation of 9·73, and dissolved in alcohol (5·67 per cent. solution) a molecular rotation of 8·62. Hydrogen chloride gives the same rotation whether dissolved in water or in amyl ether. The experiments, however, are not quite satisfactory, as a considerable portion of the amyl ether is converted into amylic chloride and amyl alcohol by the action of the hydrogen chloride.

The rotation of mixed salt solutions may be calculated from the rotations of the components, except in cases where complex salts, such as $2KI,HgI_2$, are formed. J. W.

Mercurial Thermometer for Temperatures up to 550°. By M. v. Recklinghausen (*Ber.*, **26**, 1514—1517).—The thermometer is made of Jena glass, No. 59III, and contains compressed carbonic anhydride. The author has made a number of determinations of the boiling points of sulphur, mercury, and of various organic compounds; the corrected numbers agree tolerably closely with the values obtained with the air thermometer. In the second part of his paper, the author records a number of experiments to decide the question of the existence of sulphides of phosphorus; mixtures of red phosphorus and sulphur in the proportions represented by $P_2 + S_5$, $P_2 + S_3$, $P + S_2$ respectively, were distilled; in general the boiling points showed a tendency to rise slowly. The values were for $P_2 + S_5$, 522·5—525°; for $P_2 + S_3$, 545—546·5°; for $P + S_2$, 516—519°. The subject is being further investigated. J. B. T.

Mercurial Thermometers to register up to 550°. By A. Mahlke (*Ber.*, **26**, 1815—1818).—The space above the mercury in these thermometers is filled with carbonic acid gas at a pressure of about 20 atmospheres. Their indications are accurate for temperatures up to 550°, but above this point the glass begins to soften, and the capacity of the bulb is increased by the internal pressure. The glass used in the construction is the variety of Jena glass known as 59III. In order to avoid the uncertainties of calculation in estimating the correction to be applied to these instruments for exposure of the stem, which may under certain circumstances amount to as much as 40°, the author recommends the use of a specially constructed thermometer with a long capillary mercury chamber which is placed close to the stem of the pressure thermometer. A. H.

Specific Heat of Water. By Bartoli and Stracciati (*Ann. Chim. Phys.* [6], **29**, 285—288).—The authors adopt as unity the specific heat of water at 15°. The total heat absorbed between 0° and $t°$ by unit weight of water is given by the formula

$$Qt = 1·00663t - 0·000296981t^2 + 0·000001446217t^3 + 0·00000010638t^4 - 0·000000000564t^5.$$

The mean specific heat is obtained by dividing by t, and the true

specific heat by differentiating. The differences between the calculated and experimental values do not amount to 0·00005.

A. R. L.

Heats of Combustion of Gaseous Hydrocarbons. By BERTHELOT and MATIGNON (*Compt. rend.*, **116**, 1333—1339).—The carefully purified hydrocarbons were burnt in the calorimetric bomb by means of compressed oxygen. The values obtained are as follows:—

		Hydrogen.	Carbonic oxide.	Methane.	Acetylene.
Heat of combustion ...	const. vol.....	68·15 Cal.	67·9	—	—
	const. press...	68·99 „	68·2	213·5	315·7
Heat of formation.....		—	+26·1	+18·7	+58·1

		Ethylene.	Ethane.	Propane.	Allylene.	Propylene.	Trimethylene.
Heat of combustion ..	const. vol...	340·05	370·9	526·7	472·4	497·9	505·6
	const. press.	341·1	372·3	528·4	473·6	499·3	507·0
Heat of formation.....		−14·6	+23·3	+30·5	−52·6	−9·4	−17·1

The difference between the heats of combustion of two homologous and contiguous hydrocarbons is practically constant, the value being about 157 Cal. The corresponding difference between the heats of formation is about 5·5 Cal. It follows that in the methane series the heats of combustion at constant pressure are 213·5 + 157·5*n*, in the ethylene series 341·2 + 157·5*n*, and in the acetylene series 315·5 + 157·5*n*, whilst the corresponding heats of formation are respectively +18·7 + 5·5*n*, −14·6 + 5·5*n*, and −58·1 + 5·5*n*.

The conversion of a member of the acetylene series into the corresponding olefine develops about 43·3 Cal., and the conversion of the olefine into the paraffin develops +39 Cal.

The heat of combustion of trimethylene does not agree with the view that it is a closed chain hydrocarbon. The heat of formation of trimethylene dichloride, +4·3 Cal., shows that the substitution of Cl_2 for H_2 produces a thermal disturbance similar to that observed in the methane series.

C. H. B.

Heat developed by the Combination of Bromine with Non-saturated Compounds of the Paraffin Series. By W. LOUGUININE and I. KABLUKOV (*Compt. rend.*, **116**, 1197—1200).—The experiments were made in the laboratory vessel devised by Berthelot, the substance being dissolved in carbon tetrachloride in order to moderate the reaction. The compounds used were trimethylene, boiling at 38—38·5°; hexylene, boiling at 68—68·5°; diallyl, allyl alcohol, and allyl bromide, and the results obtained were as follows:—

$C_5H_{10} + Br_2 = C_5H_{10}Br_2$	develops	+27285	Cal.
$C_6H_{12} + Br_2 = C_6H_{12}Br_2$	,,	+28843	,,
$C_6H_{10} + 2Br_2 = C_6H_{10}Br_4$	,,	+56114	,,
$C_3H_6 + Br_2 = C_3H_6Br_2O$	,,	+27732	,,
$C_2H_5Br + Br_2 = C_3H_5Br_3$	,,	+26695	,,

With diallyl, the compound $C_6H_{10}Br_2$ is formed simultaneously with the compound $C_6H_{10}Br_4$; with allyl alcohol, a notable quantity of hydrogen bromide is formed; with allyl bromide, combination takes place more slowly than in the other cases.

The authors conclude (1) that the heat of combination with bromine, in a homologous series, increases with the molecular weight of the hydrocarbon; (2) that when hydrogen has already been partially displaced by bromine, combination with this halogen takes place more slowly; and (3) when the hydrocarbon already contains a hydroxyl group, the reaction is no longer distinct, but combination is accompanied by substitution. C. H. B.

Boiling Points and Melting Points of Sulphur Compounds. By Miss A. G. Earp (*Phil. Mag.* [5], **35**, 458—462).—From tables containing a large number of organic compounds, it is shown that the substitution of sulphur for oxygen in a compound always raises the boiling point, except in those cases in which the oxygen of a hydroxyl group is replaced by sulphur, and then the reverse effect is observed. Very few exceptions to this rule exist. The same general rule is stated to hold with regard to the melting points of oxygen and sulphur compounds, but exceptions are not rare, particularly in the case of the more complicated compounds. J. W.

Heat of Vaporisation of Hydrogen Chloride. By K. Tsuruta (*Phil. Mag.* [5], **35**, 435—439).—The author has calculated the heat of vaporisation of hydrogen chloride, using the formula of Clausius, and the data of Ansdell, Biot and Arago, and Regnault. The values $dp/d\mathrm{T}$ were deduced from the following interpolation formula:—

$$p = 28{\cdot}451 + 0{\cdot}4914t + 0{\cdot}012463t^2.$$

The heat of vaporisation is 61·02 Cal. at 4°. It then increases to nearly 66 Cal. at 14°, after which it falls steadily and slowly to 35·79 Cal. at 44·8°, the fall then becoming rapid, so that the heat of vaporisation vanishes entirely at 51·25°, the critical point, the value at 49·4° being still 23·5 Cal. J. W.

Heat of Vaporisation of Organic Compounds. By H. Jahn (*Zeit. physikal. Chem.*, **11**, 787—793).—The author has determined the heat of vaporisation of various organic compounds at 0° by means of Bunsen's ice calorimeter. The following table contains his results, L being the heat of vaporisation in gram-calories, and

$$c = \mathrm{L}(k-1)/d^2\sqrt{k(k+2)},$$

where k is the dielectric constant, and d the density.

	L at 0°.	C.
Methylic acetate	113·86	30·92
Ethylic formate	113·25	30·76
Ethylic acetate	102·14	30·20
Propylic formate	105·37	30·85
Ethylenic chloride	85·40	11·99
Ethylidenic chloride	76·77	12·34
Benzene (liquid)	107·63	25·83
Pentane	74·89	28·99
Hexane	89·16	31·99
Hexylene	92·46	34·21
Methyl alcohol	292·22	58·23
Ethyl alcohol	229·04	52·01

It will be observed that the value of c for analogous substances varies very little, and the author shows that, except in the case of the alcohols, it is for any one substance practically independent of the temperature. J. W.

Critical Constants of some Organic Compounds. By M. Altschul (*Zeit. physikal. Chem.*, **11**, 577—597).—The author has determined directly the critical temperature θ and pressure π of a number of organic compounds, and from the data so obtained has calculated the critical volume ϕ and the constants a and b of the Van der Waals' formula. The results are contained in the following table.

	θ.	π.	ϕ.	a.	b.
Pentane	187·1°	33·3	0·01958	0·03829	0·00653
Hexane	234·5	30·0	0·02449	0·05395	0·00816
Octane	296·4	25·2	0·03324	0·08351	0·01108
Decane	330·4	21·3	0·04264	0·11624	0·01421
Benzene	290·5	50·1	0·01596	0·03827	0·00532
Toluene	320·6	41·6	0·02051	0·05244	0·00684
Ethylbenzene	346·4	38·1	0·02354	0·06339	0·00785
Orthoxylene	358·3	36·9	0·02487	0·06852	0·00829
Paraxylene	344·4	35·0	0·02572	0·06945	0·00857
Metaxylene	345·6	35·8	0·02517	0·06795	0·00839
Propylbenzene	365·6	32·3	0·02912	0·08212	0·00971
Isopropylbenzene	362·7	32·2	0·02904	0·08147	0·00968
Mesitylene	367·7	33·2	0·02836	0·08012	0·00945
Pseudocumene	381·2	33·2	0·02901	0·08396	0·00967
Isobutylbenzene	377·1	31·1	0·03098	0·08947	0·01033
Paracymene	378·6	28·6	0·03400	0·09921	0·01133

In addition to the above, the critical temperatures only of the following were determined: Amylene, 208·0°; hexylene, 243·5° (?); octylene, 304·8°; diamylene, 341—342°; chlorobenzene, 362·2°. H. C.

Vapour Pressures of Fatty Acids. By H. Landolt (*Zeit. physikal. Chem.*, **11**, 633—644).—Discrepancies between the results

obtained by Schmidt for the vapour pressures of the fatty acids and those of the author have led the latter to repeat his determinations. He finds that a number of his former results, those applying to pressures at low temperatures, were undoubtedly too high, and has obtained new values which are intermediate between the previous ones and those of Schmidt. Tables of these values are given in the paper. The error is attributed to the method employed for making the determinations, measurement of the tension in barometer tubes over mercury, and is due to the extreme difficulty of completely removing all air from the tube. The author considers that the dynamical is to be preferred to the statical method of determining vapour pressures. H. C.

Internal Pressure in Solutions. By G. TAMMANN (*Zeit. physikal. Chem.*, **11**, 676—692).—From the change in the temperature of maximum density of water and different salt solutions by increased pressure, the author calculates the difference between the internal pressure (constant K of Laplace) of the pure water and that of the water in the solutions. The internal pressure is always higher in the case of the solution than in that of water, and the difference being known, it is possible to calculate changes in volume on compression of the solutions, or volume changes attending the dissolution of salts in water. H. C.

Cryohydric Quintuple Points. By W. MEYERHOFFER (*Monatsh.*, **14**, 177—185).—The author considers the conditions of equilibrium in a saturated solution of a double salt, AB, with one common ion, when in contact with the salt in the solid state. Such a system will have a cryohydric point, K_D, at which the saturated solution freezes. In addition to the solution of the double salt, two other saturated solutions are possible, those of AB + A and AB + B. In the first A > B, and in the second B > A. These solutions also have cryohydric points, K_{D+A} and K_{D+B}. Each of these latter points is a quintuple point with five phases, in which five equilibria curves, corresponding each to four phases, meet. The author discusses the general character of the above curves, with the exception of the two belonging to the three solid phases and vapour, and the three solid phases and solution. H. C.

The Freezing Point of Dilute Solutions of Sodium Chloride. By H. C. JONES (*Ber.*, **26**, 1633—1639).—A controversial paper, in answer to Pickering.

Labile Conditions of Equilibrium in Salt Solutions. By A. BLÜMCKE (*Zeit. physikal. Chem.*, **11**, 645—656).—Theoretical considerations, on a thermodynamical basis, of certain special cases of labile equilibrium in solutions of hydrated salts. H. C.

Volume Changes in Aqueous Solutions. By M. ROGOFF (*Zeit. physikal. Chem.*, **11**, 657—660).—The volume changes which water undergoes when different salts are dissolved in it in equivalent pro-

portions with the formation of dilute solutions are found, on comparison, to be additive functions of the ions present in the salts. The changes are calculated from the numbers given by Ostwald for the specific volumes of certain salt solutions, 1 kilo. of each solution containing 1 gram equivalent of the base or acid present. Thus, in the case of potassium nitrate, the equivalent of which is 101·1, the water used is 2000 − 101·1 = 1898·9 grams. After dissolution, the volume of the resulting solution is 1937·3 c.c., so that the change in the volume of the water is 1937·3 − 1898·9 = 38·4 c.c. Other volume changes are calculated in like manner. The differences between the volume changes on dissolving two salts of two different bases, but one and the same acid, are independent of the nature of the acid, and if the same two bases be always taken, are constant. If two different acids with one and the same base be taken, a similar relationship holds, the differences between the volume changes being then independent of the nature of the base. A few exceptions to this rule, noticed in the case of arsenates, phosphates, and oxalates, are probably due to hydrolytic dissociation. In the case of several salts, the differences in the volume changes are very nearly equal to the differences in the molecular volumes of the dry salts, thus:

Difference in volume change.....	KCl − NaCl = 10·4.	$NaNO_3$ − NaCl = 11·2.
Difference in molecular volume	KCl − NaCl = 10·5.	$NaNO_3$ − NaCl = 10·5.

H. C.

Electrolytic Dissociation of Water. By G. Bredig (*Zeit. physikal. Chem.*, **11**, 829—831).—The author finds that the dissociation constant (K) of aniline at 25° is 11×10^{-7}, and from this result, together with the conclusions drawn by Arrhenius from the conductivity of aniline acetate solutions, calculates that the quantity of hydrogen or hydroxyl ions contained in a litre of pure water is $0{\cdot}6 \times 10^{-6}$ gram equivalents. This number agrees well with those recently found by Ostwald, Wijs, and Arrhenius. J. W.

Hydrolysis in Aqueous Salt Solutions. By J. Shields (*Phil. Mag.* [5], **35**, 365—388).—When a salt, such as potassium cyanide, formed by the combination of a feeble acid with a strong base, is dissolved in water, it is partially hydrolysed into free acid and free base, the water playing the part of a feeble acid which displaces a portion of the hydrocyanic acid from its combination with the potash. The reaction is a balanced one, so that in different degrees of concentration the amount of hydrolysis varies. The quantity of free base in the solution cannot be estimated by methods depending directly on neutralisation, but it may be ascertained by determining the rate at which the solution saponifies an ethereal salt such as ethylic acetate. The constant of velocity of the saponification is, at any given temperature, proportional to the concentration of free alkali. Since, however, fresh quantities of alkali are supplied from the continued decomposition of the potassium cyanide, as the original quantity is used up in the process of saponification, it is necessary to allow for this by the law of mass action in the construction of the equations, which

assume somewhat different forms according as the salt is little or much hydrolysed.

The author has investigated a number of salts according to this method, and arrives at the following conclusions :—

1. The amount of hydrolysis in $\frac{1}{10}$ molecular normal solutions at 24—25° is as follows :—

Potassium cyanide.....	1·12 per cent.
Sodium carbonate	3·17 „
Potassium phenoxide.....	3·05 „
Borax (about).....	0·5 „
Sodium acetate	0·008 „

Trisodium phosphate is almost entirely hydrolysed into sodium hydroxide and disodium hydrogen phosphate, which is not itself appreciably decomposed.

2. When the salts are not hydrolysed to a great extent, the amount of free alkali in the solutions is nearly proportional to the square root of the concentration.

3. The presence of varying quantities of ethylic acetate does not materially disturb the equilibrium between the salt and water on the one side and the acid and base on the other. J. W.

The Number of Saturated Solutions of a Double Salt. By W. MEYERHOFFER (*Monatsh.*, **14**, 165—175; compare Abstr., 1892, 1145).—The system $CuCl_2 + NEt_4Cl + H_2O$ has been examined, the system being capable of forming *two* double salts, $CuCl_2,2NEt_4Cl$ (M) and $5CuCl_2,2NEt_4Cl$ (P). Curves are given in which temperatures are plotted as abscissæ, and as ordinates the ratio, in molecules, of $CuCl_2 : NEt_4Cl$ in the saturated solution; this ratio is indicated by Cu/N. Up to 15·5°, three saturated solutions can exist at each temperature, containing respectively (1) M + NEt_4Cl, (2) M, (3) M + $CuCl_2,2H_2O$. From 15·5° to 31·9° four saturated solutions are possible, containing (1) M + $NEtCl_4$, (2) M, (3) M + P, and (4) P + $CuCl_2,2H_2O$. Above 31·9° five, containing (1) M + NEt_4Cl, (2) M, (3) M + P, (4) P, and (5) P + $CuCl_2,2H_2O$. Above a certain undetermined temperature, M will become incapable of existing by itself in solution, and we should then have four saturated solutions, (1) M + NEt_4Cl, (2) M + P, (3) P, and (4) P + $CuCl_2$. And above a yet higher temperature, also undetermined, the three following saturated solutions would be possible, (1) P + NEt_4Cl, (2) P, and (3) P + $CuCl_2$. Each of the five saturated solutions mentioned above is thus seen to be capable of existence only between fixed limits of temperature; the values of the ratio Cu/N, corresponding with these limits, are given below for the five solutions; they are at once evident on inspection of the curves. (1) M + NEt_4Cl, $Cu/N < \frac{1}{2}$; (2) M, $Cu/N = \frac{1}{2}$; (3) M + P, $\frac{5}{2} > Cu/N > \frac{1}{2}$; (4) P, $Cu/N = \frac{5}{2}$; (5) P + $CuCl_2$, $Cu/N > \frac{5}{2}$. Finally, the following rule is enunciated: "If two salts containing a common ion form at a given temperature n double salts, the latter and their components will at this temperature form at least $n + 1$, at most $2n + 1$, saturated solutions of different composition." C. F. B.

The Existence of Double Salts in Solution. By C. E. Linebarger (*Amer. Chem. J.*, **15**, 337).—The author submits mixtures of two salts to the action of various organic liquids, one of the salts being insoluble in the liquid. If both salts are found to pass into solution in a simple molecular ratio, the conclusion is drawn that a double salt has been formed in the solution. When a mixture of mercuric chloride and sodium chloride is acted on by ethylic acetate, in which sodium chloride is insoluble, both salts dissolve, in the proportion of 2 mols. $HgCl_2$: 1 mol. NaCl. This ratio is constant for temperatures from 0° to 50°, but at 140° the double salt decomposes, and sodium chloride is deposited. The existence of the double salt in solution is also proved by the fact that the addition of sodium chloride to a boiling solution of mercuric chloride in ethylic acetate does not raise the temperature of the boiling point. Analogous phenomena are observed with the same mixture of salts and acetone, with the chlorides of mercury and lithium and ethylic acetate, and with potassium or sodium chloride when mixed with cadmium bromide or iodide and treated with acetone or ethylic acetate.

A. H.

Conditions of Chemical Equilibrium. By S. Bugarszky (*Zeit. physikal. Chem.*, **11**, 668—675).—Yellow mercuric oxide is dissolved, to some extent, by a salt solution, or, better still, by a solution of potassium bromide. In the latter case, the action takes place in accordance with the equation $2KBr + HgO + H_2O = 2KOH + HgBr_2$. This reaction is evidently of a reversible character, and will take place in the direct or reverse sense until conditions of equilibrium are established. The ordinary laws of mass action should hold in this as in other cases, and the author shows that, as a matter of fact, the establishment of equilibrium does take place after a certain period of time, and, further, that the active mass of the solid mercuric oxide may be regarded as constant. On the other hand, the product of the active masses on the right side of the equation divided by the product of the active masses on the left, which should be constant when equilibrium is established, is found to vary within wide limits, increasing rapidly with the dilution of the solutions. This exceptional behaviour may be explained, if it is assumed that it is not the whole mass of the dissolved salts which is active in promoting the above reaction, but only that portion which has undergone electrolytic dissociation, the reaction taking place in the sense of the equation $2\overset{+}{K} + 2\overset{-}{Br} + HgO + H_2O \rightleftharpoons HgBr_2 + 2\overset{+}{K} + 2\overset{-}{OH}$, and the mercuric bromide further undergoing partial dissociation, $HgBr_2 = \overset{+}{HgBr} + \overset{-}{Br}$. In the author's experiments, the dissociation of the potassium salts in the solutions used may be regarded as complete, but that of the mercuric bromide increases with the dilution. The exceptional behaviour above recorded accords with this view.

H. C.

Affinity Coefficients of Aromatic Amidosulphonic acids. By F. P. Ebersbach (*Zeit. physikal. Chem.*, **11**, 608—632).—The

affinity coefficients of the following acids were determined, from the electrical conductivity of their solutions:—

Acid.	Affinity coeff. K.
$HSO_3 \cdot C_6H_4 \cdot NHMe$ [= 1 : 4]	0·0665.
$HSO_3 \cdot C_6H_4 \cdot NMe_2$ [= 1 : 3]	0·0353.
$HSO_3 \cdot C_6H_3(NH_2) \cdot NO_2$ [= 1 : 2 : 4]	0·85.
$HSO_3 \cdot C_6H_2Cl_2 \cdot NH_2$ [= 1 : ? : ? : 3]	0·16.
$OH \cdot C_6H_3(NH_2) \cdot HSO_3$ [= 1 : 2 : 4]	0·00941.
$OH \cdot C_6H_3(NH_2) \cdot HSO_3$ [= 1 : 4 : 2]	0·000831.
$OH \cdot C_6H_3Cl(NH_2) \cdot HSO_3$ [= 1 : 2 : 4 : 6]	0·00822.
$HSO_3 \cdot C_6H_3Me \cdot NH_2$ [= 1 : 4 : 3]	0·0250.
$HSO_3 \cdot C_6H_3Me \cdot NH_2$ [= 1 : 3 : 2]	0·0753.
$HSO_3 \cdot C_6H_3Me \cdot NH_2$ [= 5 : 1 : 2]	0·0850.
$HSO_3 \cdot C_6H_3Me \cdot NH_2$ [= 6 : 1 : 3]	0 00408.
$HSO_3 \cdot C_6H_3Me \cdot NH_2$ [= 2 : 1 : 4]	0·0357.
$HSO_3 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$ [= 1 : 4]	0·00234.
$HSO_3 \cdot C_6H_2MeBr \cdot NH_2$ [= 1 : 4 : ? : 3]	0·14.
$HSO_3 \cdot C_6HMeBr_2 \cdot NH_2$ [= 1 : 4 : ? : ? : 3]	3·0.
$HSO_3 \cdot C_6H_2MeBr \cdot NH_2$ [= 1 : 6 : ? : 3]	0·45.
$HSO_3 \cdot C_6H_2Me(NH_2)_2$ [= 1 : 5 : 2 : 4]	0·0215.
$HSO_3 \cdot C_6H_2Me(N_2H_3) \cdot NO_2$ [= 1 : 5 : 2 : 4]	0·013.

Several of the monosulphonic acids of the two naphthylamines were also examined, with the following results:—

α-Naphthylamine.		β-Naphthylamine.	
Acid 1 : 2....	K = 2·20		
„ 1 : 4....	0·20		
„ 1 : 5....	0·0240	Acid 2 : 5....	K = 0·00940
„ 1 : 6....	0·0195	„ 2 : 6 (?)	0·0166
„ 1 : 7....	0·0227	„ 2 : 7....	0·0102
„ 1 : 8....	0·00102	„ 2 : 8....	0·0122

H. C.

General Method of Chemical Synthesis. By R. Pictet (*Compt. rend.*, **116**, 1057—1060).—The author has shown in a former paper (this vol., ii, 112) that all chemical action ceases at temperatures below −130°. It is, however, possible to produce chemical action in a mass cooled to this temperature by furnishing to it energy from the outside, in the form, for instance, of electric sparks. The quantities of energy supplied in this manner may be taken as equivalent to the endothermic phase of the reaction, and the heat lost by radiation to the surroundings as a measure of the exothermic phase. With the knowledge of these two quantities, the exact conditions necessary for effecting any particular chemical synthesis could be accurately ascertained and defined. H. C.

The Atomic Weights of Stas. By J. D. Van der Plaats (*Compt. rend.*, **116**, 1362—1367).—A criticism of the discussions of Stas's results by Ostwald, and, more especially, by Hinrichs (this vol., ii, 163, 277). C. H. B.

Conservation of Mass in Chemical Changes. By H. LANDOLT (*Ber.*, **26**, 1820—1830; and more fully in *Zeit. physikal. Chem.*, **12**, 1).—The author has carried out an extended series of experiments to ascertain (1) whether any change in weight occurs when two substances react chemically. Such a change might be due either to a change in the effect of gravity, or to an alteration of the mass, produced either by the interference of the ether, or by some other unknown cause. (2) Whether, if such a change does occur, its magnitude is sufficient to account for the deviation of the experimentally found atomic weights of the elements from the whole numbers required by Prout's hypothesis. The reactions are carried out in sealed glass vessels, of almost precisely equal weight and volume. These were of such a shape that the reagents could be gradually brought into contact after the vessels had been sealed. The difference of weight of the two vessels was then determined, the reaction allowed to proceed in one of them, the difference in weight again determined, and, finally, the reaction carried out in the second vessel and the difference again ascertained. The reactions chosen were, (1) the action of silver nitrate on ferrous sulphate in aqueous solution; (2) the action of hydriodic acid on iodic acid in aqueous solution; (3) the action of iodine on sodium sulphite in solution; (4) the action of caustic soda on chloral hydrate; and, finally, (5) the solution of solid chloral hydrate in water. Using from 100 to 200 grams of reacting substances, and with apparatus weighing from 670—990 grams, it was found that a greater accuracy than 0·1—0·2 milligram could not be depended upon; changes of this magnitude occurring in opposite directions in the course of a single series of experiments. Within these limits, no difference between the weights of the vessels before and after the reactions could be ascertained. In reaction (1), a loss of about 0·1 milligram per 100 grams of reacting substance was always observed, the effect of which, even if it were accepted as a definite change of weight, would only be to increase the atomic weight of silver by 0·0009. The results obtained, therefore, confirm those previously arrived at by Stas (*Nouv. Rech.* (1865), 152, 171, 189), and, more recently, by Kreichgauer (*Verh. physik. Gesellsch., Berlin*, **10**, No. 2, 13), the latter of whom employed the same method as the author. A. H.

New Laboratory Apparatus. By O. N. WITT (*Ber.*, **26**, 1694—1698).—The author describes a laboratory press and a stirrer; the former differs from those in ordinary use, in the fact that the substance to be pressed is placed between two blocks of glazed porcelain, the faces of which are ribbed; the lower one is surrounded by a rim provided with a spout for the separation of the expressed liquid; the upper block is fitted with an iron cap, fastened with india-rubber, to receive the end of the screw. The blocks are unacted on by chemicals, can be readily cleaned, and will withstand considerable pressure.

The stirrer consists of a pear-shaped glass bulb, 20—25 mm. in diameter; the top end is fused to a glass rod, the other is open; the bulb is pierced with four holes, each the size of the open end, and arranged symmetrically around its greatest diameter; it is operated

by a turbine, at a speed of 5000 turns per minute, in the ordinary manner.

Liquids of very different specific gravity may be intimately mixed by means of this instrument, without any danger of loss, even when the vessel is almost full. J. B. T.

New Tap for Vacuum Desiccators. By O. Ernst (*Ber.*, **26**, 1698—1699).—The tap is made from a tube in the form of a Latin cross, the side pieces serving as handles; one of the longer limbs is drawn out so as to admit of being fitted to a pump; the other limb is sealed at the end and blown to a conical bulb, which is ground to fit the desiccator. At one side is a small hole, and, by turning the tap, this can be made to coincide with a depression in the socket of the desiccator, and thus establish communication with the outside air. The author recommends the use of a mixture of lanoline with a little vaseline as a suitable lubricant. The advantages of this form of tap over those generally in use are not specially apparent. J. B. T.

Inorganic Chemistry.

Molecular Weight of Hydrogen Peroxide. By W. R. Orndorff and J. White (*Amer. Chem. J.*, **15**, 347).—See this vol., i, 579.

Hydrogen Bromide. By A. Gassman (*Chem. Centr.*, 1893, i, 771; from *Schweiz. Woch. Pharm.*, **31**, 107—109).—Hydrogen bromide is readily prepared by adding bromine (385 grams) to a mixture of liquid paraffin (500 grams) and dry phosphorus in small pieces (50 grams); water (about 100 grams) is then gradually run in and the evolved gas purified by passage over moist phosphorus.

J. B. T.

The Densities of Certain Gases and the Composition of Water. By A. Leduc (*Compt. rend.*, **116**, 1248—1250).—The author discusses the agreement or otherwise between the results obtained by Regnault, Jolly, Rayleigh, and himself for the densities of nitrogen, oxygen, and hydrogen. His value for nitrogen, 0·97203, differs from that obtained by Rayleigh, 0·97209, by an amount smaller than the experimental error. He contends that Rayleigh's results simply show that the ratio of the densities of hydrogen and oxygen lies between 15·912 and 15·856, and that there is no proof that the ratio is 15·882. Further, in the case of hydrogen, the lower numbers are the more probable, whilst the reverse would seem to be true for oxygen. Critical examination of the results obtained by Rayleigh, Morley, Scott, and the author himself, leads to the conclusion that the volume ratio of hydrogen and oxygen in water is greater than 2·0032, and that the atomic weight of oxygen is most probably 15·83 when H = 1.

C. H. B.

Formation of Ozone at High Temperatures. By O. Brunck (*Ber.*, **26**, 1790—1794).—It has long been known that oxygen made from a mixture of potassium chlorate and manganese dioxide has an intense odour, resembling that of chlorine, and numerous statements have been made as to the amount of chlorine present in the gas. If chlorine is really produced in the reaction, free alkali must also be formed, and should be found as such in the residue or in the form of potassium manganate. The aqueous extract of the residue is, however, always completely neutral and colourless, and the gas evolved still has the power of liberating iodine from potassium iodide after washing with potash; it appeared therefore probable to the author that this property is really due to the presence of ozone. Experiments with ozonised oxygen showed that the ozone is not completely converted into oxygen at the temperature of the decomposition of potassium chlorate, provided it is only exposed to that temperature for a short time. The gas evolved from the potassium chlorate and manganese dioxide oxidises alcohol to aldehyde, but loses its odour and oxidising properties when passed over a short layer of manganese dioxide, and the source of these properties must, therefore, be ozone. The ozone thus formed appears, however, to differ to some extent from ordinary ozone; thus, its odour is almost exactly the same as that of chlorine, it is more stable towards heat, does not affect the surface of mercury, and attacks organic substances, such as caoutchouc, much less readily than the ozone obtained in the usual manner.

Absolutely pure potassium chlorate yields no ozone, but the presence of a trace of silica, or other indifferent compound, brings about the formation of ozone. A mixture of equal parts of manganese dioxide and potassium chlorate yields a gas containing 0·3 per cent. of ozone, the amount of the latter increasing with an increase in the proportion of dioxide, until with 25 times as much dioxide as chlorate the quantity of ozone amounts to 1·55 per cent.

In order to ascertain, if possible, the part played by the manganese dioxide in the reaction, the author has examined the behaviour of this and numerous other oxides at high temperatures. The investigation, although not yet complete, shows that the oxides examined may be divided into three classes: first, those which are quite indifferent, such as the oxides of iron, copper, and zinc; second, those which, on heating to their temperature of decomposition in an atmosphere free from oxygen, yield ozone, the amount of which is increased by heating them in a stream of oxygen, but disappears altogether when the oxide is heated with potassium chlorate; this group contains silver oxide, mercuric oxide, lead dioxide, and probably barium peroxide. The oxides of the third group give no ozone in absence of oxygen, but yield considerable quantities of it when heated to their temperature of decomposition in the latter gas, and also evolve ozone when heated with potassium chlorate at temperatures considerably below the point of decomposition of the salt; to this group belong manganese dioxide, cobalt oxide, and probably nickel sesquioxide. In all cases the presence of alkalis completely prevents the formation of ozone, and if sodium carbonate be added to the mixture the residue contains sodium peroxide. H. G. C.

Note.—The author makes no reference to the work of MacLeod (Trans., 1889, 184). H. G. C.

Plastic Sulphur from Sulphur Vapour. By J. Gal (*Compt. rend.*, **116**, 1373—1375).—When sulphur vapour is condensed on the cold surface of a liquid (compare Abstr., 1892, 1150), the elasticity of the product varies with the conditions. Water, nitric and hydrochloric acids, and solutions of sodium and potassium hydroxides and sulphurous acid at 0° give practically the same result, the product containing 45 per cent. of insoluble sulphur. With sulphuric acid, the proportion of insoluble sulphur is as high as 75 per cent., whilst with ammonia it is as low as 15 per cent. In the last case the product is not soft, but forms brittle plates. There is, however, no relation between the elasticity of the product and the proportion of insoluble sulphur that it contains; the sulphur condensed on the surface of a block of ice is very elastic, but only 20 per cent. of it is insoluble.

Experiments were made on the influence of the temperature of the sulphur vapour and the temperature of the liquid on which it condenses. For one and the same condensing liquid, the proportion of insoluble sulphur is higher the higher the temperature of the sulphur vapour. With sulphuric acid and sulphur vapour at 300°, variation in the temperature of the acid between 0° and 160° has no influence on the insolubility of the product. With sulphur vapour at 440° and sulphuric acid, or with sulphur vapour at 300° or 440° and water, or liquid sulphur at 440° and water, the proportion of insoluble sulphur in the product is higher the lower the temperature of the condensing liquid.

If the flame of hydrogen sulphide or carbon bisulphide is allowed to impinge on the surface of a cold liquid, the hydrogen or carbon burns before the sulphur, and the latter is condensed in a plastic condition. C. H. B.

Basic Metallic Sulphites. By K. Seubert and M. Elten (*Zeit. anorg. Chem.*, **4**, 44—95).—The reaction which occurs when equivalent aqueous solutions of sodium sulphite and of a metallic salt are mixed in equal proportions has been studied, the former solution being poured into the latter. The solutions usually contained 1 mol. or $\frac{1}{10}$ mol. per litre, and the reaction took place at the ordinary temperature, but, especially when the normal sulphite was obtained under these conditions; efforts were made to obtain a more basic one by carrying out the precipitation at 100° instead of at 15°, or by boiling the precipitate of normal sulphite with water. In some cases, from iron onwards, solutions containing more than 1 mol. per litre were also used, and heated together at 100° in a sealed tube. The sulphite was usually obtained as a precipitate, rarely crystallised; it was washed with water, sometimes, if readily soluble in water, with alcohol, as also when it oxidised readily, in which case the washing was carried out in an atmosphere of hydrogen, and the ratio only of metal to sulphurous acid determined in the moist precipitate; combined water could not, of course, be then determined. The metal in the precipitate was estimated in the usual way; the sulphurous acid was determined by adding the precipitate to excess of standard iodine solution and titrating the excess of the latter with thiosulphate; or by

heating it with hydrochloric acid and a weighed quantity of potassium chlorate, and estimating the amount of chlorine evolved by means of the iodine which it liberated from potassium iodide, the amount by which this fell short of that theoretically obtainable from the chlorate being the amount used up in oxidising the sulphite to sulphate; or, finally, by oxidising the precipitate with a hydrochloric acid solution of bromine, and weighing the sulphate formed as barium sulphate. The combined water was not estimated directly. Below are given the formulæ of the compounds obtained; they are, in some cases, only approximately true. Carbonates were sometimes prepared, in order to compare their composition with that of the sulphites obtained under similar conditions; their formulæ are given in brackets. Except where indicated, the compounds were not obtained crystallised.

Copper.—$4CuSO_3,3Cu(OH)_2 + 5H_2O$; when boiled with water this yields Chevreul's salt, $Cu_2SO_3,CuSO_3 + 2H_2O$ (cryst.). *Silver.*—Ag_2SO_3.

Beryllium.—$2BeSO_3,9Be(OH_2) + 6H_2O$ [$BeCO_3,5Be(OH)_2 + 3H_2O$]. *Magnesium.*—$MgSO_3 + 6H_2O$ (cryst.); $11MgSO_3,2Mg(OH)_2 + 22H_2O$(?). *Calcium.*—$CaSO_3 + \frac{1}{2}H_2O$ (cryst.). *Strontium.*—$SrSO_3 + \frac{1}{2}H_2O$ (cryst.). *Barium.*—$BaSO_3$ (cryst. ?).

Zinc.—$8ZnSO_3,7Zn(OH)_2 + 7H_2O$; $5ZnSO_3,8Zn(OH)_2$ (compare Abstr., 1891, 1157). *Cadmium.*—$CdSO_3 + 2H_2O$ (cryst.). *Mercury.*—$HgSO_3,Na_2SO_3$ (+ H_2O ?).

Aluminium.—$Al_2(SO_3)_3,3Al_2(OH)_6 + 9H_2O$ [$Al_2(CO_3)_3,5Al_2(OH)_6 + 9H_2O$; also $2Al_2(CO_3)_2,3Al_2(OH)_6 + 28H_2O$].

Thallium.—Tl_2SO_3.

Tin.—$SnSO_3$ (or $16SnSO_3,Sn(OH)_2$?). *Lead.*—$PbSO_3$.

Bismuth.—$(BiO)_2SO_3,3Bi(OH)SO_3 + H_2O$; also in ratio 3 : 7 : 10, 2 : 3 : 2, 4 : 1 : 5, and 9 : 1 : 2; [$(BiO)_2CO_3 + \frac{1}{2}H_2O$].

Chromium.—$Cr_2(SO_3)_3,2Cr_2(OH)_6 + 6H_2O$; $8Cr_2(SO_3)_3,7Cr_2(OH)_6 + 54H_2O$. *Uranium.*—$(UO_2)_2SO_3 + 4H_2O$ (cryst.); $5(UO_2)_2SO_3,3UO_2(OH)_2 + 10H_2O$ [$3(UO_2)CO_3,5UO_2(OH)_2 + 6H_2O$].

Manganese.—$MnSO_3 + 3H_2O$; $5MnSO_3,2Mn(OH)_2 + 8H_2O$ and $+ 11H_2O$.

Iron.—$FeSO_3 + 3H_2O$ (cryst.) and $+ 2H_2O$; $2Fe_2(SO_3)_3,7Fe_2(OH)_6$; $Fe_2(SO_3)_3,3Fe_2(OH)_3$ [$Fe_2(CO_3)_3,29Fe_2(OH)_6$]. *Cobalt.*—

$$5CoSO_3,Co(OH)_2 + 10H_2O;$$

$10CoSO_3,Co(OH)_2 + 15H_2O$. *Nickel.*—$2NiSO_3,Ni(OH)_2 + 6H_2O$.

It will thus be seen that silver, calcium, strontium, barium, cadmium, and mercury (as a double salt), thallium, lead, and iron (ferrous) form normal sulphites under all circumstances; magnesium, zinc, tin (stannous), uranium (uranyl), and manganese form normal sulphites under some conditions, more or less basic ones under others; and copper, beryllium, aluminium, bismuth, chromium, iron (ferric), cobalt, and nickel always form basic sulphites. There is a general similarity to the carbonates, but the latter have even a greater tendency to form basic salts; for instance, basic carbonates of lead, mercury, and, perhaps, silver, are obtained by double decomposition, although the sulphites formed under similar circumstances are normal.

C. F. B.

Absorption of Hydrogen Selenide by Liquid Selenium at a High Temperature. By H. Pélabon (*Compt. rend.*, **116**, 1292—1295).—When selenium is heated in a sealed tube containing hydrogen, hydrogen selenide is formed, and, as the tube cools, the melted selenium gives off some gas which it had absorbed at the higher temperature. Direct analysis shows that this gas contains a considerable proportion of hydrogen selenide. If some selenium, after heating in the manner described, is powdered under water, and the latter is rapidly filtered and then exposed to the air, it becomes red, owing to the separation of selenium by the action of the oxygen of the air on the dissolved hydrogen selenide. C. H. B.

Double Halogen Compounds of Tellurium with Potassium, Rubidium, and Cæsium. By H. L. Wheeler (*Zeit. anorg. Chem.*, **3**, 428—440).—A series of salts of the general formula $2RHl,TeHl_4$, in which R = K, Rb, or Cs, and Hl = Cl, Br, or I. The method of preparation consists in all cases in adding the aqueous alkali haloïd to a solution of telluric haloïd in weak haloïd acid, an excess of the latter being present to prevent the decomposition of the salt by the water, and consequent precipitation of tellurous acid. The relative proportion of the haloïds is in most cases immaterial. The salts are all soluble in weak solutions of the corresponding haloïd acid, but are precipitated from these solutions by the addition of stronger acid. With the exception of the potassium double bromide and iodide, all are anhydrous, and crystallise in regular octahedra. The cæsium iodide, however, is amorphous. The two hydrated salts, with $2H_2O$, crystallise, the bromide in orthorhombic, the iodide in monoclinic, form. The chlorides are yellow, the bromides orange to scarlet, and the iodides black.

Potassium tellurichloride, except in the presence of a large excess of telluric chloride, tends to carry down potassium chloride with it, and this circumstance has led previous workers to erroneous formulæ. It is deliquescent. The *rubidium* and *cæsium* salts are both stable in air. *Potassium telluribromide* crystallises in anhydrous octahedra when its solution is evaporated quickly, but in hydrated orthorhombic crystals with $2H_2O$ when the evaporation is spontaneous. The hydrated salt is liable to enclose mother liquor, causing the analytical results for water of crystallisation to appear too high. The *rubidium and cæsium salts* are both stable in air. *Potassium telluriodide* forms black, hydrated, monoclinic prisms with $2H_2O$; $a:b:c = 0{\cdot}7047:1:0{\cdot}5688$; $\beta = 59°\ 7'\ 16''$. Unlike the bromide and chloride, it does not form an anhydrous salt. The *rubidium salt* crystallises in microscopic octahedra, but the *cæsium salt* is amorphous, and somewhat unstable in air. Jn. W.

Crystalline Nature of Red Phosphorus. By J. W. Retgers (*Zeit. anorg. Chem.*, **3**, 399—403).—Seeing that red phosphorus occasionally assumes a sandy form, it seems not improbable that it may be crystalline. This supposition is confirmed by examination under the microscope and in polarised light. The smallest and thinnest particles are distinctly transparent, although, owing to their

high refractive power, most of the light, with the exception of a central red glimmer, is internally reflected. When, however, the phosphorus is moistened with a highly refractive liquid, such as methylenic iodide, to diminish the internal reflection, the particles transmit a clear, ruby-coloured light. In polarised light, these show extinction in two mutually perpendicular planes, and it is thus tolerably certain that they are crystalline, for the refractive power is too great to be accounted for by the assumption of internal stress in an amorphous medium. There is, however, no appreciable pleochroïsm. The crystalline system has not been determined, for although a few short prisms were observed, there were no rectilinear edges from which the system could be deduced.

Since the black or "metallic" variety of phosphorus, prepared by Hittorf (*Ann. Phys. Chem.*, **126**, 217) by heating red phosphorus to 500° and then dissolving it in, and recrystallising it from, melted lead, transmits red light, and has a sp. gr. (2·34) appreciably the same as that of the red variety (2·19), but distinctly different from that of the yellow variety (1·83), and as, moreover, the first two substances unite also in their low electrical resistance and their infusibility in offering a contrast to the last, it is not improbable that the black variety is merely a better crystallised form of the red variety, bearing somewhat the same relation to it that precipitated calcium carbonate bears to calc-spar. The black colour may be due to impurities, such as arsenic phosphide or metallic lead. JN. W.

Note.—The author entirely ignores Pedler's investigations (Trans., 1890, 599).—[EDITORS.]

Red Phosphorus. By W. MUTHMANN (*Zeit. anorg. Chem.*, **4**, 303—304).—Retgers (preceding abstract) has denied the amorphous character of red phosphorus. The author points out that red phosphorus is dimorphous, and that the commercial product is frequently a mixture of the crystalline and the amorphous forms. When vitreous phosphorus is heated in an atmosphere of carbonic anhydride at 230° for 24 hours, the product is for the most part amorphous, but crystalline in places. If the experiment is performed in a glass tube, a sublimate of amorphous red phosphorus is formed, and is readily distinguished from the crystalline portion, which does not sublime, by its bright orange-red colour, the crystals having a violet tint; the greater ease with which it may be pulverised is also characteristic. In its optical properties this sublimate maintains its amorphous character. Inasmuch as the sublimed portion should, in the author's opinion, be accounted purer than the rest, it appears that the presence of impurities, for instance arsenic, favours the formation of crystals (compare Troost and Hautefeuille, this Journal, 1873, 599; 1874, 769). A. G. B.

Phosphorus Sulphides. By M. v. RECKLINGHAUSEN (*Ber.*, **26**, 1514—1517).—See this vol., ii, 443.

Normal Thiophosphates. By E. GLATZEL (*Zeit. anorg. Chem.*, **4**, 186—226; compare Abstr., 1892, 413).—The normal thiophos-

phates are prepared by heating either the chlorides or sulphides of the metals with phosphorus pentasulphide; in the former case thiophosphoryl chloride is also produced. The process is conducted in all cases in a manner similar to that prescribed for the preparation of antimony thiophosphate (Abstr., 1892, 413).

Attempts to prepare sodium, ammonium, barium, strontium, and calcium thiophosphates proved futile; the potassium salt could not be purified from phosphorus pentasulphide.

Zinc, nickel, lead, stannous, bismuth, cuprous, and silver thiophosphates were prepared from the corresponding chlorides and phosphorus pentasulphide; *manganese, thallous, mercuric,* and *arsenic thiophosphates* were better obtained from the corresponding sulphides and phosphorus pentasulphide. Attempts to prepare the ferric, stannic, cupric, and mercurous salts by the action of phosphorus pentasulphide on anhydrous ferric chloride, stannic sulphide, cupric chloride or cupric sulphide, and mercurous chloride, respectively, resulted in the production of iron pyrites (Abstr., 1890, 338) and stannous, cuprous, and mercuric thiophosphates respectively.

The formation of a thiophosphate from phosphorus pentasulphide and a metallic chloride or sulphide appears to take place more readily the more negative the metal.

Manganese, zinc, ferrous, nickel, cadmium, and cuprous thiophosphates are crystalline powders; lead, thallium, stannous, bismuth, silver, mercuric, antimony, and arsenic thiophosphates are fusible substances which crystallise as they solidify. The manganese salt is green; the zinc and cadmium salts are white; the ferrous, nickel, lead, stannous, and bismuth salts are more or less black; the thallous, cuprous, silver, antimony, arsenic, and mercuric salts are red, the last-mentioned being very sensitive to light. The powder of the lead salt is yellowish-green, that of the stannous salt is yellow, and that of the bismuth salt reddish-brown.

The thiophosphates impart a livid appearance to the colourless bunsen flame, and evolve sulphurous anhydride when heated in air. When heated in absence of air, mercuric and arsenic thiophosphates can be distilled unchanged; lead, thallous, stannous, bismuth, silver, and antimony thiophosphates melt easily without apparent decomposition, whilst zinc, ferrous, nickel, cuprous, and cadmium thiophosphates decompose into the corresponding metallic sulphides and phosphorus pentasulphide. Nickel sulphide is left by the decomposition of the thiophosphate in the form of yellow crystals of a metallic appearance.

Solvents have no effect on the thiophosphates; dilute acids partially decompose them with evolution of hydrogen sulphide; nitric acid oxidises and dissolves them; alkalis are for the most part without action on them. The impure potassium thiophosphate evolves hydrogen sulphide when in contact with water. A. G. B.

Compounds of Arsenic Trioxide with Sulphuric Anhydride. By A. Stavenhagen (*Zeit. angw. Chem.*, 1893, 283—284).—During the repair of a pyrites furnace, Redemeister noticed several large, transparent crystals which rapidly vanished in contact with the air, yielding sulphuric acid and a residue of arsenic trioxide. It was

therefore only with some difficulty that a few undecomposed pieces could be selected and subjected to analysis, which showed the compound to have the formula $As_2O_3(SO_3)_3$. Reich has described a similar product, which, however, had the formula $As_2O_3SO_3$. Weber has described a compound prepared by heating a mixture of arsenic trioxide with sulphuric anhydride at 100° which has the same composition as the crystals analysed by the author.

When arsenic trioxide is warmed with fuming sulphuric acid, it readily dissolves, and on cooling fine needles are deposited which, according to Schulz-Sellac, have the formula $As_2O_3(SO_3)_3 + SO_3$. (The author, however, failed to confirm this formula.) When a solution of the oxide in common sulphuric acid was evaporated, there was but little volatilisation of arsenic, and the syrupy liquid, after cooling, formed a vitreous mass of the same composition.

When evaporating a solution of arsenic trioxide in sulphuric acid until no more sulphuric fumes were given off, the author also obtained a vitreous mass, but of the composition As_2O_2,SO_3. It is therefore beyond doubt that arsenic trioxide, like the corresponding antimony compound, behaves towards the stronger acids as a base.

L. DE K.

Manufacture of Borax. By H. N. WARREN (*Chem. News*, **67**, 244—245).—An intimate mixture of well-ground common salt and boric acid is introduced into an acid-proof, tubulated clay retort, and heated to slightly above a low red heat, when sufficient superheated steam is admitted through the tubulure to condense the hydrochloric acid which is evolved, the acid being collected in a cooled receptacle attached to the retort neck. Ultimately anhydrous borax only is left in the retort, and this is thrown, while still hot, into cold water and crystallised.

D. A. L.

New Alkali Borates. By A. REISCHLE (*Zeit. anorg. Chem.*, **4**, 166—177; compare Le Chatelier, Abstr., 1892, 404).—*Lithium orthoborate*, $Li_2H_4B_2O_6 + 14H_2O$, was prepared by mixing aqueous solutions of boric acid, and of lithium oxide made by igniting the nitrate in hydrogen, and evaporating to crystallisation in a vacuum. It forms thin, hexagonal tables, which are described in detail in the paper, together with the method of analysis. The water of crystallisation is lost at 110°, the remainder at 160°. *Lithium metaborate*, $LiBO_2$, is obtained on precipitating an alcoholic solution of lithium ethoxide with an alcoholic solution of boric acid, as a white, crystalline precipitate which retains alcohol when dried in a vacuum.

Rubidium borate, $Rb_2B_4O_7 + 6H_2O$, was prepared by Reisig (*Annalen*, **127**, 33); the author has confirmed his statements, and has also prepared the anhydrous *tetraborate*, $Rb_2B_4O_7$, by precipitating an alcoholic solution of rubidium oxide with a similar solution of boric acid.

Cæsium borate, $Cs_2B_8O_{10}$, is prepared in the same way as rubidium tetraborate; it separates slowly from the alcoholic solution as a white, crystalline precipitate.

A. G. B.

Volatilisation of Silica. By P. SCHUTZENBERGER (*Compt. rend.*, **116**, 1230).—The volatilisation of silica observed by Moissan

explains certain facts previously observed by the author, namely, that when pure silica is heated at a high temperature in a gas-carbon crucible brasqued with lamp black, there is a distinct loss of weight; and that when platinum is strongly heated it increases in weight, becomes fusible, and contains silicon, even though it is separated from siliceous matter by a layer of carbon. Silicon, on the contrary, seems to be non-volatile. C. H. B.

Combustion of Carbon in Air. By R. Ernst (*J. pr. Chem.* [2], **48**, 31—45).—The course of the formation of carbonic oxide in a producer was studied by heating coke in a porcelain tube through which a current of air was passing, and analysing the products of combustion. An arrangement is figured and described in the paper, by means of which the gases can be collected, without undue contact with water, in Hempel's burettes, and subsequently analysed over mercury. The methods of analysis are detailed. The length of the layer of coke, the temperature, and the rate of passage of the air were varied in the different sets of experiments. The temperature was measured by a Le Chatelier platinum | platinum-rhodium pyrometer.

Tabulation of the conditions and results shows, in the author's opinion, that the composition of the products of combustion depends almost exclusively on the temperature. The formation of carbonic anhydride begins at about 400°, and at this temperature there is already a small quantity of carbonic oxide produced. The maximum production of carbonic anhydride occurs at about 700°, and amounts to some 20 per cent. of the products (including the nitrogen of the air used); up to this temperature the formation of carbonic oxide is but small, hardly exceeding 3 per cent.; the oxygen, however, is entirely used. At higher temperatures, the carbonic anhydride rapidly disappears, giving place to carbonic oxide, until at 995° this gas amounts to 34 per cent., the remainder being atmospheric nitrogen. It must be noted, however, that the rate of passage of the air was much reduced in those experiments in which the highest temperatures were maintained; no reason is assigned for this. There was no further change in the composition of the products up to the highest temperature (1092°) at which the author experimented. The production of carbonic oxide could not be induced at a lower temperature by altering the other experimental conditions.

It is concluded that carbonic oxide is the only oxidation product of carbon at 1000°, and that producer gas should be prepared at this temperature. By substituting carbonic anhydride for air, it was proved that this gas is never entirely reduced to carbonic oxide by the hot fuel, so that, where the production of carbonic oxide is preceded by that of carbonic anhydride, some of this gas must appear among the products of combustion; it may be concluded, therefore, that the carbon burns directly to carbonic oxide.

In the rational furnace, where a high temperature is required, the air supplied directly to the fuel must be only sufficient to burn it to carbonic oxide, which must subsequently be burnt by admission of fresh air. The temperature must be maintained at 995° and upwards.

The observation that coke burns without flame at moderate temperatures, but with flame at higher temperatures, is now explicable.

A. G. B.

Action of Oxygen on Sodammonium and Potassammonium. By A. Joannis (*Compt. rend.*, **116**, 1370—1373).—When pure and dry oxygen is passed into a solution of sodammonium or potassammonium in liquid ammonia at about $-50°$, the oxygen is rapidly absorbed, and the colour of the solution first becomes blue-black, and then the colour gradually disappears. With care, the quantity of oxygen required to decolorise the solution can be ascertained. The ammonium derivative is converted into a gelatinous precipitate resembling aluminium hydroxide.

The product from sodammonium is a white powder with a rosy tint, and it dissolves in water with great development of heat, but without any evolution of gas. It has the composition NH_3,Na_2O or NH_2Na_2OH. The compound NH_2Na_2Cl has previously been obtained by the action of sodium chloride on sodammonium.

By prolonged action of oxygen on the ammonia solution, a rose-coloured product, Na_2O_3, is obtained; this, when treated with water, evolves oxygen, and yields the hydrated dioxide described by Vernon Harcourt. Both the compounds NH_3,Na_2O and Na_2O_3 form at the beginning if the current of oxygen is too rapid.

In the case of potassamonium, if the current of oxygen is slow, the product at the moment of decolorisation is K_2O_2, a rose-coloured, gelatinous precipitate. If the passage of the oxygen is continued, the colour of the precipitate changes to brick-red, and at the moment when this colour is deepest the product has the composition K_2O_3. Further action of the oxygen changes the colour to chrome-yellow, and the ultimate product is K_2O_4.

The dioxide dissolves in water, and yields a somewhat stable solution with powerful oxidising properties. The tetroxide also dissolves in water, with abundant evolution of oxygen. With a very small quantity of water, the dioxide reacts violently and even explosively, and seems to split up into the tetroxide and metallic potassium. C. H. B.

Water as a Catalyst. By R. E. Hughes (*Phil. Mag.* [5], **35**, 531—534).—Silver chloride, prepared in the dark, dried perfectly in an air-bath, and then placed on a watch-glass in a desiccator partially exhausted, was found not to be perceptibly darkened in sunlight, even after an exposure of some hours; whereas a rapid darkening took place when moisture was introduced. Paper, when moistened with potassium iodide solution and exposed to the light, assumes a brownish-violet tint. As the staining varies very greatly with different kinds of paper, being greatest with highly-glazed note-paper, the author attributes it to the presence in the paper of chlorine.

When dry hydrogen chloride was passed over dry silver nitrate, either at the ordinary temperature or at 100°, it was found that only about 1 per cent. of the theoretical change had taken place after two hours. Hydrogen chloride acts on dry manganese dioxide, whether moisture is excluded or not.

Dried hydrogen chloride only produces a slight turbidity with a

solution of silver nitrate in hot, dry benzene or ether. With absolute alcohol as solvent, the amount of precipitate obtained is somewhat greater. Mercuric chloride in absolute alcohol forms a greenish-yellow precipitate with dried hydrogen sulphide only after a long time.

When dry ammonia and dry hydrogen chloride are mixed, they do not combine (compare Baker, Proc., 1893, 129). J. W.

Atomic Weight of Barium. By T. W. Richards (*Zeit. anal. Chem.*, **3**, 441—471).—Barium bromide was eventually found to be the most suitable barium compound for the estimation of the atomic weight. The method finally adopted consisted in determining the equivalents of barium bromide in terms both of free silver and of silver bromide. Full details are given of the purification of the various substances used.

In the actual analysis, the barium bromide was gradually heated to redness, and the anhydrous salt weighed and dissolved in water, the slight amount of hydroxide and carbonate formed during the ignition being neutralised and estimated by standard hydrobromic acid. A solution of a known weight of silver in nitric acid, prepared in accordance with Stas's directions, was then added in the usual way, and the excess of silver or bromine determined by titration, the end point being repeatedly estimated both by direct and backward titration. In some cases, the bromide was added to the silver, a method of procedure which tended to increase the difference between the two end points without, however, altering their mean value. To furnish the data for the second series of determinations, the silver bromide was washed by decantation, collected in a Gooch crucible, dried (in some cases fused), and weighed. In certain cases, the barium bromide was used in the hydrated state, a concurrent determination of moisture being made on an approximately equal quantity.

The mean result of some 19 analyses gives the ratio $Ag : BaBr_2 = 1 : 1{\cdot}37749$ and the ratio $AgBr : BaBr_2 = 1{\cdot}7408 : 1{\cdot}37749$. The percentage of silver in silver bromide thus incidentally determined is 57·446 against Stas's number 57·445.

Taking Ag = 107·93 and Br = 79·955, the atomic weight of barium is thus from the first ratio 137·426, with a maximum deviation of +0·030 and −0·040 from the mean; and from the second ratio 137·431, with a maximum deviation of ±0·054. Taking Ag = 107·66 and Br = 79·955, these numbers become 137·083 and 137·089 respectively. The difference between these numbers and those yielded by the older classical determinations is due partly to the improvements in analytical methods effected by Stas, and partly to improved methods of purification. Jn. W.

Copper Oxybromide analogous to Atacamite. By J. Dupont and H. Jansen (*Bull. Soc. Chim.* [3], **9**, 193—195).—Brun (Abstr., 1889, 1112) prepared an oxybromide of copper analogous to atacamite which appeared to form quadratic crystals, an observation which is surprising in view of the fact that atacamite crystallises in the orthorhombic system.

The authors prepare the oxybromide $CuBr_2,3CuO + 3H_2O$ by heating a solution of cuprous bromide with copper oxide in a sealed tube at 200°, or, better, by heating neutral dilute solutions of cuprous bromide at 225°; the green crystals obtained by the second method are found to be rhombohedral plates; their sp. gr. is 4·39. The constitution of atacamite and this compound is discussed, and from a study of their behaviour on heating (when they lose two-thirds of their water at 200° and the remainder at 250°), the authors submit, under reservation, the constitutional formulæ $OH{\cdot}Cu{\cdot}O{\cdot}Cu{\cdot}Cl + H_2O$ and $OH{\cdot}Cu{\cdot}O{\cdot}Cu{\cdot}Br + H_2O$ for atacamite and its bromine analogue.

A. R. L.

Metallurgy of Lead. By J. B. Hannay (*Chem. News*, **67**, 291).—It is found that, by simply melting and crystallising, all mixtures of lead and lead sulphide may be fractionated into metallic lead and lead monosulphide. This compound has, according to the author, a sp. gr. 7·766, and forms a series of volatile compounds with both carbonic anhydride, with carbonic oxide, with water, and with sulphurous anhydride, which are only stable at a red heat. The reaction $PbS + PbSO_4 = 2Pb + 2SO_2$ usually given as representing a reaction going on when lead is smelted in a reverberatory furnace is shown to be incorrect, inasmuch as when lead sulphide and lead sulphate react, the volatile compound PbS_2O_2 is formed. A minute study of the furnace reactions of lead and its oxide, sulphate, and sulphide has led to the conclusion that lead smelting is a fractionation of a low sulphide into lead and its sulphide with the formation of an oxysulphide, PbS,PbO, which is the basis of black and grey slags. As a result of these investigations, a new metallurgy of lead has been devised in which the production of the slag-forming oxysulphide is avoided, and the volatile oxysulphide is utilised; whilst any silver can be eliminated, and any proportion of lead, its sulphate or oxide, can be formed directly from galena. During the fractionation of a low sulphide of lead into the metal and the monosulphide, a curious crystalline form of lead sulphide is produced. A new method of analysing lead sulphide has been devised by the author.

D. A. L.

Graphochemical Calculation. By E. Nickel (*Zeit. physikal. Chem.*, **11**, 598—607).—The author applies the method of calculation described in previous papers to the reactions involved in the reduction of lead ores.

H. C.

Action of Liquid Chlorine on Metallic Chlorides. By A. Classen and B. Zahorski (*Zeit. anorg. Chem.*, **4**, 100—110).—Compounds of lead tetrachloride have been prepared for the first time in the pure state. A solution of *lead tetrachloride* is obtained by digesting a mixture of the dichloride with liquid chlorine and fuming hydrochloric acid for 30—40 hours in a mixture of ice and salt. If ammonium chloride is added to this solution, a compound,

$$2PbCl_4,5NH_4Cl,$$

is obtained; it forms a lemon-yellow powder, turns orange when heated, and decomposes above 120°. It is decomposed by a small quan-

tity of water yielding lead dichloride, hypochlorous acid (and chlorine?), whilst with a large quantity of water, or with alkalis, it yields lead dioxide. If quinoline hydrochloride is used instead of ammonium chloride, a compound, $PbCl_4,2(C_9NH_7,HCl)$, is obtained. This has the same general characters as the ammonium compounds, but is more stable; with cooled solutions of bromide and iodide of potassium, it yields the bromide, $PbBr_4,2(C_9NH_7,HBr)$, as a red powder, and the iodide, $PbI_4,2(C_9NH_7,HI)$, as a brownish-black powder; these compounds decompose readily, and lose bromine or iodine respectively, when treated with alcohol and ether. A pyridine compound,

$$2PbCl_4,5(C_5NH_5,HCl),$$

of a similar character was also prepared. Compounds of lead dichloride with pyridine hydrochloride, $3PbCl_2,4(C_5NH_5,HCl)$, and with pyridine, $3PbCl_2,4C_5NH_5$, were prepared for the sake of comparison; they crystallise in colourless needles. Finally, it seems probable that a cobalt compound, $Co_2Cl_6,10C_5NH_5,2CoCl_2$, was obtained in the same way as the pyridine compound of lead tetrachloride. C. F. B.

Mixed Double Haloïds of Lead and Potassium. By C. H. Herty (*Amer. Chem. J.*, **15**, 357; compare Abstr., 1892, 779, and this vol., ii, 278).—The mixed double iodides and bromides of lead and potassium have been found (this vol., ii, 278) to be, as a rule, mixtures of the double salts $KPbI_3,xH_2O$ and $KPbBr_3,xH_2O$. When, however, the amount of lead iodide is made small in proportion to the bromide (less than 1 : 4 parts by weight), the crystals obtained from a solution of the two salts in a strong solution of potassium bromide (2 to 3 of water) contain at the most a trace of iodine, and have the formula K_2PbBr_4,H_2O. This salt has been previously obtained by Wells (*Amer. J. Sci.*, **45**, 132), and is formed along with that of the formula $KPbBr_3,H_2O$, when lead bromide is dissolved, without the addition of bromine, in a strong solution of potassium bromide. A. H.

Approximate Determination of the Equivalents of Earths by Titration. By G. Krüss and A. Loose (*Zeit. anorg. Chem.*, **4**, 161—165).—The method consists in precipitating the rare earths by the addition of an excess of oxalic acid, filtering, and titrating the filtrate with potassium permanganate solution. It was proved that none of the oxalate remains in solution. The results obtained corresponded in every case with an equivalent higher than that obtained by conversion into sulphate in the ordinary way, and it is noted that in order to bring the two equivalents into agreement, it is necessary to multiply that obtained by titration by the factor $\frac{8}{7}$; the conclusion seems to be warranted that the cerium and yttrium earths form oxalates consisting of 17 equivalents of base combined with 16 equivalents of oxalic acid. There are difficulties to be overcome in obtaining confirmatory evidence of the above conclusion by direct analysis of the oxalates; these are being combated. It appears that in the case of the yttrium earths the oxalate approaches the normal in composition more nearly the greater the purity of the earth; on the

other hand, the tendency of the ytterbium earths is to form oxalates more basic than is represented by the ratio 17 : 16. The method may be useful for rapid determinations if the solution of the earth be not too acid, and the excess of oxalic acid used be reasonably small.

A. G. B.

Anhydrous Chlorides of Metals of the Rare Earths. By O. Pettersson (*Zeit. anorg. Chem.*, **4**, 1—9).—These were prepared by placing the mixture of oxides, obtained by working up a rare earth, in a tube of gas carbon, itself inclosed in a porcelain tube, and heating it to a white heat in a current of dry hydrogen chloride. Chlorides of the composition MCl_3 volatilise into the front part of the tube, and hydrogen and carbon monoxide are evolved; a small quantity of oxychloride and oxide remain behind. The carbon must act as the reducing agent, although it is only in contact, and not intimately mixed, with the oxide, for if the latter be placed in a platinum tube it is no longer reduced by hydrogen chloride. The chloride from nearly pure yttrium oxide forms a white, silky, laminated, crystalline mass; that from cerium oxide, a white powder; those from xenotime (a gadolinite mineral) and impure holmium oxide, a yellowish-grey, laminated mass. Of the metals of the gadolinite group, yttrium seems to form the most volatile chloride, of the cerite metals didymium, and the chlorides of the first-mentioned group seem to be in general more volatile than those of the second.

C. F. B.

Terbia. By K. Hofmann and G. Krüss (*Zeit. anorg. Chem.*, **4**, 27—43).—That part of the mineral gadolinite which yields a yellow oxide, and has been supposed by Mosander, Delafontaine, Marignac, and De Boisbaudran to contain a distinct element, terbium, has been re-examined, the methods adopted including fractional decomposition of the nitrate by heat, fractional crystallisation of the formate and double sulphate, and fractional solution of the hydroxide in aniline hydrochloride (compare this vol., ii, 376). By this means it was shown that no fraction could be obtained with a definite atomic weight unalterable by further fractionation; hence the so-called terbia is not the oxide of a single element, but is a mixture of oxides. It is worthy of note that a fraction was obtained which could not be further decomposed by crystallisation of the double sulphate or formate, but which could yet be separated into fractions of different atomic weight by solution in aniline hydrochloride.

C. F. B.

Holmium Oxide. By K. Hofmann and G. Krüss (*Zeit. anorg. Chem.*, **3**, 407—414).—The residual earth which remains after the separation of yttrium and scandium oxides from erbia has been shown by Cleve to consist of a less basic rose-coloured portion, and a more basic yellow portion, the solution of which shows absorption bands $\lambda = 640—2$ and 536, identical with those of Soret's holmium oxide, Ho_2O_3, Ho = 160. Boisbaudran has shown that this portion is not a chemical individual, but is mixed with a more basic dysprosium oxide, whilst Crookes has further shown that the dysprosium oxide from gadolinite is itself complex, and contains holmium and other oxides. Krüss and Nilsson have arrived at a similar conclusion by a

comparative study of the spectra of the rare earths, and have found that holmium salts can be resolved into a series of fractions showing absorption bands varying in wave-length from $\lambda = 660{\cdot}4$ to $\lambda = 428{\cdot}5$.

To verify these views as to the complex nature of holmium oxide by gravimetric methods, the authors have now worked up and examined a considerable quantity of Nilsson's holmium material, consisting of oxide and of basic nitrate fractionally precipitated from the solution of the oxide. The various fractions all gave the holmium lines in exceptional strength, together with the erbium lines Er_α and Er_β, but their atomic weights varied from 139·1 to 163·6. The solution of the oxides was repeatedly fractionated with aniline hydrochloride, and eventually gave a series of identical fractions showing the holmium spectrum, and giving the atomic weight 161·6, closely agreeing with Cleve's 160. A similar preparation was made from the nitrates, and mixed with the first. The oxide thus prepared had a yellow colour, and turned white on heating with hydrogen, but without alteration of spectrum. It could not be further differentiated by fractional precipitation of the chloride with potassium sulphate, or by fractional decomposition of the nitrate by heat, so that apparently a chemical individual had been obtained. But by prolonged treatment with aniline hydrochloride, the oxide was split up into a series of fractions, in the less basic alone of which the holmium lines occurred, and the atomic weights obtained from these fractions formed a sinuous curve, which became more pronounced and at the same time more uniform in character as the fractionation proceeded, and pointed to the existence in the oxide of the two elements of atomic weights corresponding to the maxima and minima of the curves. The colour of the fractionated oxides inclined to red with increasing atomic weight. The atomic weight curve strongly resembled that yielded by erbia under similar treatment, but the constituent elements are not the same, for the absorption spectra were quite different. Moreover, the erbium oxides were obtained from feebly basic yttrium earths, whilst the holmium oxides were obtained from strongly basic yttrium earths containing a large amount of yttrium oxide. Whatever the relation may be between erbium and holmium oxides, the latter is undoubtedly a complex of two or more oxides of the yttrium group. JN. W.

Action of Heat on Zinc Permanganate. By T. KLOBB (*Bull. Soc. Chim.* [3], **9**, 105—109).—Zinc permanganate, $Zn(MnO_4)_2 + 6H_2O$, when heated slowly, loses water and oxygen, and leaves zinc manganite. At 140°, the volume of oxygen evolved corresponds with the equation $2Zn(MnO_4)_2 = 2ZnO + 4MnO_2 + 3O_2$. Heated quickly, it gives off pink vapours or, more properly, a fine dust, of manganese trioxide. This substance was obtained by heating the permanganate in an open tube, aspirating the vapours formed through sulphuric acid containing a little anhydride, and then collecting them in a glass tube packed with fragments of porcelain; not more than 0·05 gram was obtained from 10—20 grams of the permanganate. The trioxide forms small, very hygroscopic lumps of a kermes colour; moisture

colours it reddish-violet, and it decomposes at 60°, leaving a brown residue. It may be kept unchanged for a long time in a sealed tube. A determination of the metal and of the available oxygen corresponded roughly with the formula MnO_3. C. F. B.

Reduction of Ferric Salts and Solution of Ignited Ferric Oxide. By L. Storch (*Chem. Centr.*, 1893, i, 876; from *Ber. Österr. Ges. Chem. Ind.*, **15**, 9—13).—The author has investigated the action of zinc on ferric sulphate under various conditions, as he believes that the reduction is due to the direct action of the zinc and not to nascent hydrogen. In all cases considerable excess of zinc was necessary, and the action proceeded slowly. Copper in the form of thin wire gives much better results.

Ignited ferric oxide readily dissolves on warming with sulphuric acid (40 per cent.). J. B. T.

Iron Chloroborate and Chloroborates Isomorphous with Boracite. By G. Rousseau and H. Allaire (*Compt. rend.*, **116**, 1195—1197).—Chloroborates isomorphous with boracite are obtained by the action of the vapours of metallic chlorides on native calcium borate or, better, on boronatrocalcite. As a rule, crystalline products cannot be obtained by the fusion of calcium borate with chlorides.

The case of iron presents special difficulties, because ferrous chloride is not volatile at a sufficiently low temperature. Good results are, however, obtained by passing the vapour of ferric chloride over an intimate mixture of calcium borate with a large excess of small pieces of wrought iron or steel wire, the mixture being heated at about 330°. Ferrous chloride is formed, and immediately reacts with the borate. The excess of ferrous chloride is dissolved by means of water, and the unattacked iron is easily separated. The product has the composition $6FeO,8B_2O_3,FeCl_2$, a small portion of the iron being replaced by isomorphous calcium.

Iron chloroborate crystallises in greyish, transparent cubes, which act on polarised light. Natural boracite has similar special properties, and the symmetry is really pseudo-cubic. The iron compound dissolves slowly in nitric acid, and is rapidly decomposed by fused alkali carbonates.

Zinc chloride and cadmium chloride also yield pseudo-cubic boracites. C. H. B.

Cobalt. By E. Donath (*Monatsh.*, **14**, 93—108).—Pure unoxidised cobalt does not dissolve in strong, hot aqueous potash; the blue solution obtained under these circumstances with finely-divided cobalt, reduced from the oxide, is due to oxide still admixed with the metal. This blue solution does not, as several observers have stated, contain cobalt in any higher state of oxidation than that corresponding with CoO, for it does not liberate iodine from an acid solution of potassium iodide, nor does it oxidise an acid solution of ferrous ammonium sulphate. If the blue solution be allowed to remain in contact with air, it can be shown to absorb oxygen, and the dark substance which separates out has a composition intermediate between

Co_3O_4 and Co_2O_3. But since this was formed by oxidation of the substance present in the blue solution, the latter must be in a lower state of oxidation, and thus cannot possibly be CoO_3, as several observers have supposed. C. F. B.

The Elementary Nature of Nickel and Cobalt; their Atomic Weights. By C. WINKLER (*Zeit. anorg. Chem.*, **4**, 10—26).—The grounds are first discussed on which Krüss and Schmidt (Abstr., 1889, 349, 1114; this vol., ii, 212) and Remmler (this vol., ii, 211) base their conclusions that nickel and cobalt, as hitherto known, are not pure elements, and it is suggested that the variations in the atomic weights noticed by these observers were due to impurities derived from the glass vessels used. The author concludes, "I cannot believe that nickel contains a hitherto unknown substance, differing from it in properties and atomic weight; on the contrary, I regard both it and cobalt as simple substances, and elements in the present sense of the word."

The atomic weights of both elements were determined by dissolving a weighed quantity of the metal, purified by two successive electrolytic depositions in hydrochloric acid in a platinum basin, evaporating to dryness, heating the residual chloride at 150°, and estimating the chlorine in it, in one series gravimetrically, in another volumetrically by Volhard's method, six determinations being made by each method. Results: Ni = 58·8334—58·9684, mean 58·90; Co = 59·5996—59·7480, mean 59·67. [Standard not given.] The mean values are probably more accurate than the divergence of the individual results indicates. C. F. B.

Reactions with Ammonia at Low Temperatures. By O. T. CHRISTENSEN (*Zeit. anorg. Chem.*, **4**, 227—233).—Regarding the function of ammonia in the metallic ammonium compounds as similar to that of water in crystalline salts, the author argues that salts which will not combine with ammonia at ordinary temperatures should do so at low temperatures, just as salts which are anhydrous at ordinary temperatures become hydrated at low temperatures.

When liquid ammonia is brought into a beaker containing anhydrous, violet chromic chloride, cooled in a mixture of solid carbonic anhydride and ether to about −75°, there is no reaction. But when the vessel is removed from the freezing mixture, and the temperature allowed to rise nearly to the boiling point of the ammonia, a violent reaction ensues, the chromic chloride being converted into a red mass. After the odour of ammonia has nearly disappeared, the mass is washed with cold water (whereby a portion of it is dissolved with a yellow colour) until the washings show the colour of chloropurpureochromium chloride; the undissolved residue is then treated with concentrated hydrochloric acid, the acid poured off, and the still undissolved residue washed on a filter, and finally dissolved in cold water. This solution is poured into strong hydrochloric acid, whereby pure chloropurpureochromium chloride is precipitated.

The yellow, aqueous washings mentioned above yield luteochromium nitrate on the addition of strong nitric acid.

The reaction between chromic chloride and ammonia is much retarded by the presence of water, and only occurs at temperatures of a comparatively narrow range, the boiling point of ammonia being apparently the most favourable temperature.

When ferric chloride is treated with liquid ammonia, a reddish-yellow powder is obtained which is immediately decomposed by water.

Red potassium chromium chloride also yields a mixture of chrom-ammonium compounds when treated with liquid ammonia.

A. G. B.

Chromodisulphuric, Chromotrisulphuric, and Chromosulphochromic acids. By A. Recoura (*Compt. rend.*, **116**, 1367—1370).—Under the name of chromosulphates, the author has previously described (Abstr., 1892, 783) compounds of the type

$$Cr_2(SO_4)_3,M'_2SO_4.$$

Chromosulphuric acid is most easily prepared by evaporating on a water-bath a solution containing violet chromium sulphate and sulphuric acid in molecular proportion, and heating the residue at 110—120°.

Chromodisulphuric acid, $(Cr_25SO_4)H_4$, and chromotrisulphuric acid, $(Cr_26SO_4)H_6$, are obtained in a similar way, using 2 or 3 molecular proportions of sulphuric acid.

The three acids are deep green powders soluble in water in all proportions. They are quite stable in the solid condition, but gradually decompose in solution. Dilute barium chloride solution produces a greenish-white, flocculent precipitate of barium chromosulphate, but a concentrated solution of barium chloride yields a precipitate of barium sulphate. Their heats of neutralisation are greater than that of sulphuric acid.

$(Cr_24SO_4)H_2$	diss.	+ 2NaOH	diss. ...	develops	+33·3 Cal.
$(Cr_25SO_4)H_4$	„	+ 4NaOH	„ ...	„	+33 × 2 Cal.
$(Cr_26SO_4)H_6$	„	+ 6NaOH	„ ...	„	+32 × 3 „
SO_4H_2	„	+ 2NaOH	„ ...	„	+30·8 Cal.

The energy of the acid function decreases as the proportion of sulphuric acid increases.

The chromosulphates are obtained by evaporating a solution of chromic sulphate with 1, 2, or 3 molecular proportions of the particular sulphate. They are soluble in water, and their solutions are more stable than those of the free acids. Dilute barium chloride solution produces no precipitate.

The constitution of the three acids is most probably

$$(SO_4)_2Cr_2(SO_4H)_2,\ SO_4Cr_2(SO_4H)_4,\text{ and } Cr_2(SO_4H)_6.$$

Chromosulphochromic acid, Cr_23SO_4,CrO_4H_2, can be obtained by the combination of chromic sulphate with chromic acid. If the constitution attributed to the chromosulphates be correct, the constitution of this acid will be $(SO_4)_2Cr_2{<}^{SO_4H}_{CrO_4H}$, and this view is supported by

the fact that the heats of neutralisation of the two acid functions are respectively 16·0 Cal. and 12·3 Cal. C. H. B.

Sodium Perchromate. By C. Haüssermann (*J. pr. Chem.* [2], **48**, 70—72).—A salt of the composition $Na_6Cr_2O_{15} + 28H_2O$ crystallises after some time from a solution made by adding sodium peroxide to a thin paste of chromium hydroxide and water, kept at 10—20°. It forms red-brown, vitreous crystals which rapidly effloresce in the air. In dilute sulphuric acid they are rapidly decomposed, with evolution of oxygen and formation of chromium sulphate, but there is an intermediate development of the characteristic blue colour of perchromic acid. By treatment with hot water, a part of the sodium is converted into sodium hydroxide, the remainder becoming sodium chromate. The analytical numbers indicate the equation $Na_6Cr_2O_{15} + H_2O = 2Na_2CrO_4 + 2NaOH + 3O_2$ as representing the change. The author is investigating the question of the constitution of the anhydride, Cr_2O_{12}, corresponding with this salt. A. G. B.

Preparation of Tungsten, Molybdenum, and Vanadium in the Electric Furnace. By H. Moissan (*Compt. rend.*, **116**, 1225—1227).—The oxides of tungsten, molybdenum, and vanadium, metals which have hitherto proved very difficult to isolate and obtain in a fused condition, were intimately mixed with carbon, and heated in the electric furnace (this vol., ii, 167).

With a current of 350 ampères and 70 volts, an ingot of 120 grams of tungsten is obtained in about 10 minutes, and if the oxide has been present in excess, the metal is pure. It is brilliant, and very hard; sp. gr. = 18·7. If, on the other hand, the carbon is in excess, products are obtained containing a proportion of carbon which varies with the conditions from 0·64 to 6·33 per cent. These products have a brilliant fracture, are stable in presence of air, and are sometimes covered with a layer of blue tungsten oxide. At a much higher temperature (with a current of 1000 ampères and 70 volts), the proportion of carbon in the product rises to 17·27—18·81 per cent.

Molybdenum oxide, obtained by heating ammonium molybdate, yields a molybdenum carbide containing 9·77—9·90 per cent. of carbon. It has a brilliant fracture, is very hard, and scratches steel and glass, and remains unaltered in moist air; sp. gr. 8·6.

Vanadium oxide is only very slightly reduced with a current of 350 ampères and 70 volts; but with a current of 1000 amperès and 70 volts it is rapidly reduced, and yields a carbide containing as much as 25 per cent. of carbon (17·56 to 25·68); sp. gr. = 5·3.

It would seem that the higher the temperature the greater the proportion of carbon taken up. It also seems that molybdenum, uranium, tungsten, and vanadium are less fusible than chromium, their fusibility following the order given. C. H. B.

Action of Hydrogen Haloïds on Molybdic acid. By E. F. Smith and V. Oberholtzer (*Zeit. anorg. Chem.*, **4**, 236—246).—When molybdic acid is heated at 150—200° in hydrogen chloride, the com-

pound $MoO_3,2HCl$ is sublimed (Debray, *Compt. rend.*, **46**, 1098). When hydrogen bromide is substituted for the chloride, a *compound*, $Mo_2O_3Br_4$, sublimes in the form of square, permanganate-coloured plates which are unstable in air; at the same time a brownish-yellow liquid, $MoO_3,3HBr$, condenses in the tube, and crystallises in long, yellow, deliquescent needles when cold.

Hydrogen iodide begins to act on molybdic acid in the cold, iodine being liberated, and a violet-coloured substance formed, the composition of which could not be accurately ascertained. At 105—120° the product retains no iodine, and consists of the *oxide*, $Mo_4O_{10},3H_2O$, which is blue, and stable in air.

Hydrogen fluoride, at 300—400°, converts molybdic acid into a volatile, white, crystalline *oxyfluoride*, $Mo_2O_3F_4$; it is deliquescent, and easily soluble in hydrofluoric acid, but not in water. Indications of other products were obtained. A. G. B.

Phosphomolybdates. By C. Friedheim (*Zeit. anorg. Chem.*, **4**, 275—297; compare this vol., ii, 282).—The author reviews our knowledge of the constitution of the so-called phosphomolybdic acid and its salts. By the interaction of potassium dihydrogen phosphate and molybdic anhydride, there are produced several white compounds, which may be regarded as molecular aggregates of the micro-crystalline salt, $K_2O,P_2O_5,2MoO_3 + 13H_2O$, produced at a certain stage of concentration, with potassium molybdate.

When fewer than two molecular proportions of molybdic anhydride react with one of potassium monohydrogen phosphate, the compounds $5K_2O,2P_2O_5,10MoO_3,11H_2O$ and $3K_2O,P_2O_5,5MoO_3,7H_2O$ are produced. When two molecular proportions of the anhydride are used, the compounds $5K_2O,2P_2O_5,10MoO_3,20H_2O$; $2K_2O,P_2O_5,4MoO_3,8H_2O$; and $K_2O,P_2O_5,5MoO_3,6H_2O$ are formed.

Potassium phosphate reacting with molybdic anhydride in the proportion of $1P_2O_5 : 5MoO_3$ gives rise to the compounds $3K_2O,P_2O_5,5MoO_3$; $5K_2O,2P_2O_5,10MoO_3$; $2K_2O,P_2O_5,5MoO_3$; $2K_2O,P_2O_5,4MoO_3$.

The author discusses the constitution of these compounds, and describes the isolation of the sodium compounds

$3Na_2O,P_2O_5,18MoO_3,26H_2O$; $5Na_2O,2P_2O_5,48MoO_3,100(\text{or } 111)H_2O$;

and $3Na_2O,P_2O_5,18MoO_3,25H_2O$. A. G. B.

Phospholuteotungstic acid. By F. Kehrmann (*Zeit. anorg. Chem.*, **4**, 138—144).—It was found desirable, for certain reasons, to revise the work (Abstr., 1887, 777) on this acid. The acid has been found to have the composition $P_2O_5,18WO_3 + 41H_2O$; the *potassium* and *ammonium salts* are $3K_2O,P_2O_5,18WO_3 + 14H_2O$ and

$$3(NH_4)_2O,P_2O_5,18WO_3 + 14H_2O.$$

When the potassium salt is treated with potassium hydrogen carbonate at the ordinary temperature, it yields a compound

$$5K_2O,P_2O_5,17WO_3 + 22H_2O,$$

in white, satiny needles; from the ammonium salt, a compound may also be obtained, in tabular crystals, by the action of ammonium hydrogen carbonate; in it the ratio $P_2O_5 : WO_3$ also $= 1 : 17$.

The estimation of potassium in the salts of these complex acids is conveniently effected by precipitating the acid with a solution of an organic base, especially quinoline, in an acid, such as acetic, sulphuric, or hydrochloric, and determining the potassium in the filtered solution.

As a result of the comparison of many phospho- and arseno-tungstates and -molybdates, it seems that salts belonging to the four classes $3RO,P_2O_5,18MoO_3$, $3RO,As_2O_5,18MoO_3$, $3RO,P_2O_5,18WO_3$, and $3RO,As_2O_5,18WO_3$ must possess a similar structure, as also those of the three classes $3RO,P_2O_5,24MoO_3$, $3RO,As_2O_5,24MoO_3$, and

$$3RO,P_2O_5,24WO_3$$

(water of crystallisation is omitted in these formulæ). C. F. B.

Preparation of Zirconium and Thorium. By L. Troost (*Compt. rend.*, **116**, 1227—1230).—An intimate mixture of zirconium oxide and carbon, when heated in the electric arc in an atmosphere of carbonic anhydride, yields small, metallic masses, which contain 76·9 to 78·2 per cent. of zirconium and 23·1 to 21·8 per cent. of carbon, and which, therefore, approximate closely in composition to zinc carbide, ZnC_2. The product is steel-grey in colour, and is very hard, scratching glass easily, whilst it is itself unaffected by the hardest steel. If the cupel is brasqued with zirconium oxide, the proportion of carbon in the product is lower. The carbide is readily dissolved by hydrofluoric acid, even when dilute, but it is not attacked by other acids. If the proportion of carbon is low, it only oxidises superficially at a red heat, but it burns brilliantly at this temperature if it contains a high proportion of carbon. With the current used (30 to 35 ampères and 70 volts), no volatilisation of zirconium was observed. If, however, zircon is heated in the arc, silica volatilises, and condenses in long filaments.

Thorium oxide, under similar conditions, is reduced more easily than zirconium oxide, and the product contains 8·2 to 9·5 per cent. of carbon, and, therefore, approximates in composition to the carbide, ThC_2. It is less hard than the zirconium carbide, is very brittle, and scratches glass slightly; sp. gr. at 15° = 10·15. It decomposes cold water, with evolution of hydrogen mixed with strongly smelling hydrocarbons, and it gradually decomposes with intumescence when exposed to moist air. At a red heat it burns rapidly and brilliantly.

If this carbide is heated in the arc with excess of thorium oxide, it yields small, metallic masses, which do not alter when exposed to air. C. H. B.

Black Antimony Trisulphide. By C. A. Mitchell (*Chem. News*, **67**, 291).—By dissolving 5 grams of antimony trioxide in 30 c.c. of a mixture of 2 parts of hydrochloric acid and 1 of water and saturating the solution with hydrogen sulphide, then keeping it boiling while a current of carbonic anhydride is passing through, a portion of the orange sulphide dissolves, but some is precipitated as

black sulphide; by repetitions of the treatment, all the sulphide ultimately assumes the latter form, which has the composition Sb_2S_3.

D. A. L.

Double Halogen Compounds of Gold. By E. Petersen (*J. pr. Chem.* [2], **48**, 88—91).—The author maintains, in reply to Krüss and Schmidt (this vol., ii, 284), that the product of the action of chlorine, or of bromine, on gold is neither a mixture of gold and a trihaloïd, nor of a mono- and tri-haloïd, but a true aurosoauric haloïd.

A. G. B.

Action of Chlorine and Bromine on Gold. By G. Krüss and F. W. Schmidt (*Zeit. anorg. Chem.*, **3**, 421—427).—A reply to Thomsen (this Journal, 1877, ii, 485; Abstr., 1888, 559) and Petersen (this vol., ii, 126). A repetition of Thomsen's experiment on the direct chlorination of precipitated gold shows that considerably more chlorine (29·0 per cent.) is taken up than that required by the formula Au_2Cl_4 (26·5 per cent.). Petersen's results (in five different preparations, 25·7—29·1 per cent. of chlorine) indicate that he was dealing with a mixture of variable composition. On repeating his experiment, the authors find that the residue left after exhausting the product of chlorination with alcohol contains chlorine (15·96 per cent.), closely corresponding with that contained in aurous chloride (15·24 per cent.). The action of bromine on precipitated gold (5·5 grams), under Thomsen's conditions, has been further studied, with specially purified materials, with the result that the weight of the product (12·08 grams) corresponds with the weight of auric bromide (12·19 grams) required by theory. The product, moreover, is practically entirely soluble in water.

Jn. W.

Action of Silicon on Gold, Silver, Platinum, and Mercury. By H. N. Warren (*Chem. News*, **67**, 303—304).—A brittle regulus, fusible at a red heat, having a crystalline fracture, only slightly soluble in acids, and containing 10 per cent. of silicon, is obtained when graphitoïdal silicon is heated to a full red heat in contact with platinum, or when a mixture of amorphous silicon and platinum-black is heated under a layer of potassium silicofluoride in a closed crucible. By heating to a high temperature a mixture of potassium silicofluoride, sodium, and amorphous gold or silver, a silicide of the metal may be obtained. These metals alone will not combine directly with silicon, but, if in the molten state they are contaminated even with only a small quantity of the silicide obtained in the manner just described, a considerable amount of elementary silicon is readily absorbed. Silver containing 5 per cent. of silicon is as brittle as antimony, and looks like a highly argentiferous alloy of gold and silver, and when the proportion of silicon is raised to 10 per cent., silver silicide becomes slightly red, and resembles metallic manganese in appearance; when pulverised, the regulus is completely decomposed by concentrated hydriodic acid. When mercury in contact with an alcoholic solution of silicon fluoride was submitted to the action of a powerful battery, the mercury, when subsequently distilled, left a residue of a small quantity of amorphous silicon, but no silicide of mercury was isolated.

D. A. L.

Palladium Sulphides. By P. Petrenko-Kritschenko (*Zeit. anorg. Chem.*, **4**, 247—250).—The palladium sulphide prepared by precipitating a palladous salt with hydrogen sulphide always contains more sulphur than corresponds with the formula PdS. Attempts to produce this sulphide by heating potassium palladium chloride in hydrogen sulphide resulted in mixtures of the sulphides PdS_2 and Pd_2S. The author concludes that there is no certain evidence of the existence of the sulphide PdS. A. G. B.

Mineralogical Chemistry.

Iron from Ovifak. By H. Moissan (*Compt. rend.*, **116**, 1269—1271).—Several specimens of the iron from Ovifak were examined for the various forms of carbon, in the manner previously described. In one specimen, fragments of sapphire were found. Three specimens contained amorphous carbon, two of them contained intumescent graphite, one alone contained ordinary graphite, and none of them contained diamonds in any form. C. H. B.

Occurrence of Gold containing Palladium in the Caucasus. By T. Wilm (*Zeit. anorg. Chem.*, **4**, 300—302).—A gold matte from a sand rich in magnetic iron ore, from the neighbourhood of Batoum, was found to contain 8—9 per cent. of palladium. The chemical interest of the occurrence resides in the fact that the palladium is not converted into palladous chloride when the aqua regia solution of the palladiferous gold is evaporated and treated with hydrochloric acid, the presence of the gold apparently hindering the reduction. The usual indication of the presence of palladium, the red-brown colour of palladous chloride solution, being thus unattainable, this metal is liable to be qualitatively mistaken for platinum when it occurs in gold, the more so because the ammoniopalladic chloride, into which it is converted by the usual treatment with ammonium chloride, much resembles impure ammonioplatinic chloride. A. G. B.

Physiological Chemistry.

Influence of Carbonic Anhydride on the Diastatic and Peptone-forming Ferments in the Animal Organism. By N. P. Schierbeck (*Chem. Centr.*, 1893, i, 745—746; from *Skandinav. Arch. Physiol.*, **3**, 343).—The action of human saliva on various starches is increased by the presence of carbonic anhydride, except in the case of wheat-starch, which, however, behaves like the others if made slightly alkaline. In presence of acids, carbonic anhydride

either hinders or entirely prevents the fermentation. Similar results were observed in the case of invert ferment solution with cane sugar, of saliva with glycogen, and of pancreas extract with rice starch; the larger the quantity of alkali present, the greater the proportion of carbonic anhydride required to accelerate the action.

Animal diastatic ferments react most readily in acid solution, for the acidification of which hydroxypropionic acid is preferable to hydrochloric acid; the presence of 5—10 per cent. carbonic anhydride is sufficient in these cases also to hinder the fermentation. Similar results were observed with trypsin. Saliva and pancreas ferment containing trypsin, unlike pepsin, are not decomposed by carbonic anhydride; its effect on the course of the fermentations appears to be due to the acidity it produces. J. B. T.

Metabolism in a Child 14 Months old. By W. CAMERER (*Zeit. Biol.*, **29**, 227—232).—Observations on the metabolism of young children are difficult on account of the collection of urine and fæces. In the present experiment on a girl these difficulties appear to have been successfully overcome.

The experiment lasted four days. The diet was simple, consisting of milk, egg, biscuit, and water.

The amount of proximate principles may be stated thus in grams per diem:—

	Mean.	Minimum.	Maximum.
Water	1191·0	970·0	1389·0
Proteïd	31·0	25·0	38·6
Fat	21·4	17·3	27·2
Carbohydrate....	126·0	118·0	133·0

The analyses of urine are given in the following table:—

Urine.	Quantity.	Total N.	Hüfner N.	N residue.	Urea by Hüfner's method.	Uric acid by different methods.	Nitrogen in xanthine substances.
	grams	grams	grams	grams	grams	milligrams	milligrams
Of the 1st and 2nd days	850	3·47	3·15	0·32	6·755	160 to 173	3·5
Of the 3rd and 4th days	660	4·07	3·65	0·41	7·833	149 to 166	3·1
Mean of the 4 days	755	3·77	3·40	0·37	7·284	155 to 169	3·3

Taking the mean of the four days, and the total nitrogen as 100,

the nitrogen residue was 9·8, that of the uric acid 1·4, and that of the xanthine substance 0·09. Taking the urea as 100, the uric acid is a little over 2.

The small output of uric acid is noteworthy; the same was found in earlier researches in children of from 2 to 5 years of age.

W. D. H.

Metabolism during Inanition. By W. Prausnitz (*Zeit. Biol.*, **29**, 151—167).—Fifteen experiments on adult human beings are recorded in which the nitrogenous excretion was estimated during a period of inanition lasting two days. The output of nitrogen is, of course, diminished in comparison with the normal; but the chief point of interest noted is that, on the second day, the output is either practically the same as on the first, or more frequently (12 out of the 15 experiments) exceeds it—often very considerably.

The following table gives the amount of nitrogen in grams:—

Experiment.	Normal days.	First hunger day.	Second hunger day.
1	9·3 to 11·7	7·8	13·0
2	64 to 81 (? 6·4 to 8·1)	4·6	4·4
3	16·8	11·9	10·6
4	12·2	9·6	13·0
5	9·6 to 12	13·3	11·0
6	7·8 to 8·5	7·9	10·3
7	—	9·3	12·5
8	14·2 to 15·3	14·0	14·9
9	18·6	12·9	13·8
10	15·5 to 16·2	7·9	14·5
11	12·4	7·7	12·6
12	15·8 to 16·9	13·3	16·0
13	13·6 to 13·9	8·2	14·9
14	—	11·7	13·0
15	22·3 to 23·1	17·3	19·3

W. D. H.

Physiology of Starvation. By C. Lehmann, F. Mueller, I. Munk, H. Senator, and N. Zuntz (*Virchow's Archiv*, **131**, Suppl. No., 1—228).—Two very complete series of observations are recorded on two individuals who submitted themselves for experiment. In the first case, the well-known professional faster, Cetti, was starved for 10 days. In the second, a young German, named Breithaupt, was the subject of an experiment which lasted for six days. In both cases water was allowed.

The facts observed come under the following headings: (1) general condition, including exhaustive measurements of the various parts of the body; condition of pulse, with tracings; blood corpuscle counting, and body weight; (2) examination of the fæces and urine; and (3) respiratory exchange.

Observations were made daily, and the results are given in detail, and also tabulated. References are also given to other work of a similar kind, especially to Luciani's work on Succi, when the general results were much the same.

The chief facts noted are as follows:—

Weight—Cetti weighed 57 kilos. at the beginning, and 50·6 kilos. at the end of the hunger period. The loss of weight was most marked during the first half of this period. Breithaupt weighed 60 kilos. at the beginning, and 56·5 kilos. at the end of his experiment. The body measurements showed a gradual diminution in each case, and was most marked in situations where large masses of muscle and fat were present.

Circulation.—The frequency of the pulse was in Cetti's case but little altered, but arterial tension was lessened, as shown by the sphygmograph. Breithaupt's pulse became very slow (on the sixth day 47): the pulse curve, however, showed less alteration than in Cetti's case. In both cases the excitability of the heart was increased, slight exertion sending up the pulse rate. Examination of the blood showed, in the case of Cetti, a rise in the number of red and white corpuscles, but a fall in the amount of hæmoglobin. In Breithaupt's case there was a slight rise in the number of corpuscles, and in the amount of hæmoglobin also.

Fæces.—As compared with dogs and cats, the amount was small; the nitrogen in it was relatively larger than normal, although the absolute amount was small. Fat and fatty acids were abundant. The odour denoted very little putrefaction. Hydrobilirubin was present, mixed with bilicyanin.

Urine.—The quantity of urine varied with the amount of water drunk; its specific gravity was in the inverse ratio. The acidity of the urine was increased. The nitrogen excreted was diminished, but only to a small extent. This appears to be one of the most striking points noticed in the investigation. From this the amount of proteïd metabolism was estimated: the amount of proteïd decomposed daily in Cetti's case varying from 56 to 95 grams; in Breithaupt's case from 62 to 80 grams. The excretion of sulphur ran parallel to that of nitrogen. The quotient A/B (A = preformed sulphuric acid, B = combined sulphuric acid) varied in the two cases considerably. Acetone and phenol were present in considerable quantity; and traces of albumin were found in both cases; indican was absent.

The amount of chlorides sank very greatly; that of phosphates did not; and this, combined with the fact that calcium and magnesium were but little affected, suggests that the bones underwent wasting; the amount of phosphate and calcium being too great to be accounted for by muscular wasting. The amount of sodium excreted was very small, less than that of potassium.

Respiratory Exchange.—This is most carefully and exhaustively given; and again one is struck with the very small variations from the normal condition. The temperature also remained constant. The influence of work was difficult to investigate because of the early onset of fatigue, especially of the heart. But the small increase of the respiratory quotient during work excludes the possibility that carbohydrate material can be an important source of muscular power.

W. D. H.

Proteïds of Nervous Tissues. By W. D. Halliburton (*J. Physiol.*, **15**, 90—107).—The normal reaction of nervous tissues is

alkaline. This alkalinity diminishes after death, and may be replaced by an acid reaction. This is most marked in the region where there are most cells, namely, in the grey matter.

Quantitative determinations show that proteïd matter is a very important constituent of nervous structures. The average amount of proteïd in the solids of grey matter is over 50 per cent. It is less in the white matter, and also in parts like the spinal cord, which contain large quantities of white matter. It is less still in nerve. Grey matter is also the poorest in total solids; nerve the richest. In any region like the spinal cord, where there is a mixture of white and grey matter, the percentage of water, the proportion of proteïd in the solids, and the proportion of grey matter vary directly the one with the others.

The following table gives a summary of a number of analyses which illustrate this point:—

	Water.	Solids.	Percentage of proteïd in solids.
Grey matter of cerebrum.....	83·5	16·5	51
White „ „	70·0	30·0	33
Cerebellum.....	80·0	20·0	42
Spinal cord as a whole	72·0	28·0	31
Cervical region of cord.....	72·5	27·5	31
Dorsal „ „	70·0	30·0	28
Lumbar „ „	73·0	27·0	33
Sciatic nerves.....	61·0	29·0	29

Qualitative examination of this proteïd matter shows that the proteïds present are three in number, A, B, and C.

A. This proteïd is a globulin, and may be termed neuro-globulin α. It is coagulated by heat at the low temperature of 47°, and is analogous to similar globulins obtained from other cellular structures. It is precipitated by a comparatively small percentage of such neutral salts as magnesium sulphate; it is not precipitated by weak acetic acid, and contains no phosphorus in its molecule.

B. This proteïd is a nucleo-albumin. It can be readily obtained by precipitating an aqueous extract of brain with weak acetic acid. The supply obtainable from white matter is small. It is coagulated by heat at 56—60°. It is precipitable by saturating its solutions with neutral salts. It contains 0·5 per cent. of phosphorus. After subjection to gastric digestion, an insoluble residue of nucleïn remains behind. Dissolved in dilute sodium carbonate solution, and injected into the circulation of rabbits, it causes extensive intravascular coagulation.

C. This proteïd is a globulin, and may be termed neuro-globulin β. It is coagulated by heat at 70—75°. It requires complete saturation with magnesium sulphate to precipitate it entirely. Peptone, proteose, myosin, albumin, and fibrin-ferment (in Schmidt's sense) are not obtainable from nervous tissues. W. D. H.

Action of Sodium Oxalate on Voluntary Muscle. By F. S. Locke (*J. Physiol.*, **15**, 119—120).—A frog's sartorius, immersed in 0·75 sodium oxalate solution, becomes in a few seconds violently active, much more so than in Biedermann's "normal saline" solution. After 30 to 45 minutes, it loses its irritability, which, however, is partially recovered by immersion in 0·6 sodium chloride solution made with New River water.

This probably explains the symptom of fibrillary muscular contraction observed by Kobert and Küssner in sodium oxalate poisoning, and which they ascribed to an action on the central nervous system.

W. D. H.

Phloridzin Diabetes. By W. Prausnitz (*Zeit. Biol.*, **29**, 168—174).—Two experiments on dogs are recorded; in each, two similar animals were used. In one, the glycogen of the body was estimated; in the other, phloridzin diabetes was produced. The amount of sugar extracted was in great excess beyond what the glycogen in the control animal would account for. The phlorose arising from the drug would only account for quite a small percentage of the sugar excreted.

W. D. H.

Phloridzin Diabetes in Frogs. By M. Cremer (*Zeit. Biol.*, **29**, 175—176).—Phloridzin given subcutaneously produces diabetes in frogs. The sugar in the urine gave Trommer's test, and yielded crystals of phenylglucosazone.

W. D. H.

Phloridzin Diabetes. By M. Cremer and A. Ritter (*Zeit. Biol.*, **29**, 256—276).—From experiments on rabbits recorded in the present paper, and from the consideration of the work of others in the same direction, the question of the origin of the sugar produced by phloridzin is discussed. The glycogen of the body will not account for it; the sugar derived from the drug itself is also insufficient: indeed, phloridzin appears to be wholly excreted as such in the urine. Its presence renders polarimetric estimation of the sugar in the urine untrustworthy as phloridzin is lævorotatory. Further, the possible origin of the sugar or a part of it from the chondrosin of cartilage and from glucosamine is discussed, but the conclusion is arrived at that the only satisfactory explanation is that the sugar arises from the proteïd of the body. This view is confirmed in a very striking way by tables and charts, which show that the proteïd metabolism in phloridzin diabetes, as in pancreatic diabetes, runs parallel to the amount of sugar excreted. The curves of nitrogen output and sugar excretion rise and fall one with the other.

W. D. H.

Urinary Hæmatoporphyrin. By A. E. Garrod (*J. Physiol.*, **15**, 108—118).—In continuation of previous researches (Abstr., 1892, 1506), it is found that hæmatoporphyrin can generally be detected in urine; in normal urine its quantity is very small. Direct spectroscopic examination of specimens rich in hæmatoporphyrin shows that it is alkaline hæmatoporphyrin which is present.

When neutral hæmatoporphyrin is added to urine, the spectrum seen is that of the alkaline pigment, even though the urine is acid, or even

though it is made considerably more acid than normal by the addition of acid sodium phosphate. If, however, large excess of this phosphate is added, the acid spectrum appears.

Amyl alcohol extracts the pigment from urine, but it is mixed with urobilin and uroerythrin. Ethylic acetate and carbon tetrachloride also take up the pigment; chloroform only dissolves traces. In all cases it is the alkaline pigment which is obtained, but this sometimes shows an additional (fifth) band far into the red: the same is occasionally seen in the urine itself.

Some specimens deepen in tint on standing; hence the supposition that urinary hæmatoporphyrin may partially exist as a chromogen.

In some cases hæmatoporphyrin is obtainable from sediments of urates; and in other cases a pigment is obtained which appears to be a precursor of hæmatoporphyrin. Its absorption bands are similar to those of oxyhæmoglobin; it is identical with the substance obtained when hæmatoporphyrin is treated with zinc chloride and ammonia. It is unchanged by alkalis, but is at once changed into hæmatoporphyrin by mineral acids. It appears to be identical with a similar pigment isolated by Stockois by dialysis from the urine of one of his cases, and also noticed by Hammarsten. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Effront's Method for the Purification and Preservation of Yeast by means of Hydrofluoric acid or Fluorides. By A. Jörgensen and J. C. Holm (*Chem. Zeit.*, **17**, No. 23).—The authors point out that the principle of this method is the same as that of Pasteur's (Abst., 1892, 904), which consists in treating the yeast with tartaric acid, and that it is inconceivable that a single substance should only act favourably towards the one desired species of yeast and detrimentally towards all the disease germs, and all the undesirable cultivated yeasts which may be present. They show further that the development of a number of known disease germs is actually favoured by this treatment, just as Hansen proved to be the case with the tartaric acid treatment, so that such disease germs may get the upper hand and the desired cultivated yeast become suppressed.

The authors have made an elaborate series of experiments in order to practically test Effront's method, from which the following results may be quoted:—

(1) A distillery yeast, which contained *Mycoderma* in such small amount that it could be detected only with difficulty by the microscope, showed a very strong development of this impurity after treatment by Effront's method. (2) Pure cultures of *Mycoderma* and *Bacterium aceti* were added in very small quantity to a pure culture of a distillery yeast. After treatment with ammonium fluoride, the *Mycoderma* cells were found to have multiplied very freely, whilst

Bacterium aceti was by no means suppressed. In another experiment *Bacterium aceti* was found to have multiplied considerably. In an experiment with a pure brewery yeast (low) to which a very small quantity of *Mycoderma cerevisiæ* was added, the yeast was almost entirely suppressed by the latter organism. (3) A distillery yeast which gives good results in practice was mixed with 20 per cent. of a brewery yeast (low), and after treatment twice by Effront's method, the distillery yeast was *completely crowded out* by the beer yeast. (4) In another mixture of an excellent distillery yeast with a small quantity of a brewery yeast (high), *Sacch. cerevisiæ I*, Hansen, the latter yeast gained the upper hand. (5) In experiments with mixtures of the yeast known as *Carlsberg II* with small quantites of *Sacch. Pastorianus III*, Hansen, the latter, which is a disease yeast, multiplied considerably, and in one case the yeast *Carlsberg II* almost completely disappeared. Similar results were obtained with mixtures of a distillery yeast with small quantities of *Sacch. Pastorianus III*.

The above results show that treatment by Effront's method favours the development of the so-called *disease yeasts*, of *Mycoderma*, of brewery yeasts when present in distillery yeasts, and finally also of *Bacterium aceti*, and the conclusion cannot be too strongly emphasised, that the employment in practice of hydrofluoric acid and the fluorides for the purification and preservation of yeast is attended with very great danger. A. K. M.

Alcoholic Fermentation of Jerusalem Artichokes under the Influence of Pure Yeast. By L. Lévy (*Compt. rend.*, **116**, 1381—1382).—An extract of Jerusalem artichokes in water containing 0·2 per cent. of potassium hydrogen tartrate was sterilised, and then mixed with pure yeast from Romane Conti, or with a ferment resulting from a cultivation of this yeast on an infusion of barley. Fermentation takes place rapidly at 20—25°, and is complete in about three days. The chief product is ethyl alcohol of good flavour, together with a comparatively small quantity of aldehyde and a still smaller quantity of higher alcohols. In the quality of the main product and the low proportion of the head and tail products, fermentation with pure yeast has a considerable advantage over the ordinary method. C. H. B.

Assimilation of Atmospheric Nitrogen by Microbes. By S. Winogradsky (*Compt. rend.*, **116**, 1385—1388).—It is an established fact that elementary nitrogen is fixed by leguminous plants in symbiosis with microbes, and by mixtures of the lower organisms inhabiting soils, green algæ, and microbes. But the power of nitrogen fixation cannot as yet be ascribed to any particular kind. In the experiments now described, cultivations of soil organisms were made in nutritive solutions (prepared with distilled water, specially purified salts, and very pure dextrose), in closed vessels, the air of which was purified by means of potash and sulphuric acid. In each experiment, gas was liberated, and an acid (chiefly butyric) formed, and finally masses of matter were seen, formed by a large bacillus, and frequently containing spores. These bacilli were conspicuous by their normal appear-

ance and the relative richness of their development. The bacillus could not be obtained in a state of perfect purity, but the two others which remained with them were quite insignificant, and seem to be of no importance as far as the present investigation is concerned, inasmuch as they only develop in the presence of combined nitrogen.

The large bacillus resembles Fitz's *B. butylicus* in many respects, but cannot yet be stated to be identical.

The following figures show (1) the weight of dextrose employed (in grams) in the experiments, (2) the weight of nitrogen given (if any), and (3) the amount of free nitrogen fixed (in milligrams).

Experiment:	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Dextrose.	1	1	1·5	6	3	?	1	1	3	6	7
N_2 added.	—	—	—	—	—	—	—	2·1	—	—	—
N_2 fixed..	3·0	2·3	4·5	10·4	8·9	7·2	2·7	2·4	8·1	12·8	14·6

Experiment:	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.
Dextrose....	4	?	4	5	2	2	2	2	2	2
N_2 added....	2·1	2·1	2·1	3·0	—	—	—	1·8	4·0	3·3
N_2 fixed	8·4	5·6	14·3	12·5	3·1	2·9	2·5	1·7	0·6	0·8

The question arises whether there is any relation between the amount of sugar decomposed and the nitrogen fixed, whether assimilation can take place at the expense of organic matter other than sugar, such as the organic matter of soils, and what are the most favourable conditions for nitrogen fixation. N. H. M.

Assimilation of Carbonic Anhydride by Chlorophyllous Plants. By A. Bach (*Compt. rend.*, **116**, 1145—1148).—Sulphurous acid, when exposed to sunlight, decomposes with formation of sulphuric acid, water, and sulphur. In a similar manner, carbonic acid (H_2CO_3) might be supposed to decompose with formation of a compound, H_2CO_4 (which would be the acid corresponding with Berthelot's anhydride, CO_3) and formaldehyde [$H_2O + C$]. The acid, as soon as formed, would decompose, yielding carbonic anhydride and hydrogen peroxide; the presence of the latter in plants was observed by Wurster (Abstr., 1887, 295; compare also Bokorny, Abstr., 1888, 751).

The following experiments were made, the results of which, if not conclusive, are, at least, in accordance with the author's theory:—

A stream of pure carbonic anhydride was passed through two flasks, each containing a 1·5 per cent. solution of uranium acetate. One flask was exposed to direct sunlight; the other was covered with black paper to exclude light. Some more of the solution was exposed to sunlight in a closed flask. The contents of the flask containing the solution treated with carbonic anhydride and exposed to sunlight became turbid and more or less greenish in about 20 minutes; after some time, there was a considerable deposit, which, when filtered and washed, had a violet colour. This precipitate, when exposed, became yellow, and was transformed into a mixture of uranous and uranic hydroxides, with a trace of a brownish substance, probably uranium peroxide. The solutions exposed to the action of sunlight alone and of carbonic anhydride

alone remained unchanged. The reaction is explained thus: The carbonic acid would be converted into aldehyde and percarbonic acid, which would form uranium percarbonate: this would decompose into uranium peroxide and carbonic anhydride. The reduction of uranium peroxide to uranic and uranous hydroxides might be brought about by the aldehyde. A separate experiment was made, in which uranium peroxide was exposed to the action of hydrogen peroxide and formaldehyde; the yellowish precipitate acquired a greenish colour, and was finally transformed into the violet-brown substance soluble in acetic acid. N. H. M.

Condensation of Carbonic Anhydride under the Influence of Sunlight. By A. Bach (*Compt. rend.*, **116**, 1389; compare preceding abstract).—Solutions of dimethylaniline dissolved in water (20 parts), to which sulphuric acid (1 part) had been added, were exposed to sunlight under the following conditions:—No. 1, in an open flask. No. 2 was exposed in a flask through which carbonic anhydride was being passed. No. 3, like No. 2, but wrapped round with grey filter paper. After a lapse of two hours, 30 c.c. of solution was removed from each flask for examination, when it was found that in the case of No. 1 no effect had been produced; in No. 2 tetramethyldiamidophenylmethane was produced in an amount sufficient to give a very intense reaction; in No. 3 a trace of this compound was found. The result shows that the carbonic anhydride had been converted by the action of sunlight into aldehyde, which reacted with dimethylaniline, yielding the above tetramethyl compound. The reaction is of extreme delicacy, and is shown in all degrees of intensity according to the amount of light employed. An ordinary gas flame is sufficient. N. H. M.

Iron in Plants. By A. Molisch (*Bied. Centr.*, **22**, 336—338; from *Bot. Centr.*, **50**, 370).—Iron occurs in plants partly in a loose form (when it may be extracted by means of acid) and partly in closer union with the plant, so that it can only be detected in the ash. Algæ and fungi seldom contain any considerable amount of iron which may be directly extracted with acid, but large quantities are found in certain lichens. Some mosses (*Fontinalis* and *Miliachoferia*) are rich in iron. The deposits occur chiefly in the membrane, and sometimes impart a brownish colour to the older leaves. Iron is, however, not necessary for the growth of these mosses. A remarkable case of iron accumulation is the fruit shell of *Trapa natans*, the ash of which contains 68 per cent. of ferric oxide.

Insoluble iron is of very general occurrence in plants. As regards iron bacteria, the author does not attach the same importance to iron as Winogradsky, but considers it to be unnecessary for the bacteria, and of no more importance than the deposition of silica in grasses. In the examination of 34 samples of bog iron ore from various mines, there were only two cases where considerable quantities of iron bacteria were found, a result not in favour of Winogradsky's assumption that these ores were produced by the bacteria.

Carefully executed investigations on chlorophyll furnished results which indicated that chlorophyll does not contain iron. Chlorose

occurs as a symptom of a disease produced by abnormal nutrition. Iron is as necessary for fungi as for green plants. Results contrary to this were due to the fact that the nutritive solutions employed were never quite free from iron, and that fungi are able to appropriate the smallest amounts of it. N. H. M.

Migration of the Starch of Potatoes in the Tubers. By A. GIRARD (*Compt. rend.*, **116**, 1148—1151).—Prunet has already showed that the parts of sprouted tubers where the young shoots start are especially rich in starch, and that there may be a difference of as much as 4·2 per cent. in the amount of starch of sprouted and non-sprouted tubers. He concluded that during germination the nutritive matters migrate to the parts where new life is manifested. A similar migration produced by the dry weather of 1892, but much more extensive, was observed in the study of seed potatoes. The drought lasted until July (when the tubers form), and, with slight interruptions, into the middle of August. Regularly formed tubers were produced, but weighing only 50 to 60 grams. The abundant rain of the next two months caused the tubers to develop suddenly; at the top of each, the terminal bud gave rise to an often enormous shoot (increasing the weight to as much as 300 or 400 grams). On separating some of these hour-glass shaped tubers into two parts and determining the starch in both parts, a difference of as much as 12—13 per cent. was found; the original tubers played the part of seed potatoes, and gave up the greater part of their starch to the newly developed portions. This migration of starch was fully confirmed by the microscopical examination of the different parts of the tubers. Taking a section of the tubers, it was found that near the umbilicus the cells were free from starch, at half the length some grains of starch were found, whilst at the top the cells abounded in starch. Moreover, a zone was found in which the few remaining grains were undergoing solution previous to their departure. N. H. M.

Occurrence of Betaïne and Choline in Wormseed (Artemisia Gallica, Wild.). By E. JAHNS (*Ber.*, **26**, 1493—1496).—The finely-divided seeds are extracted with hot water, the solution treated with lead acetate and soda and subsequently with chloroform; the bases are then precipitated from the aqueous solution with potassium bismuthiodide in presence of sulphuric acid, the precipitate is digested with recently prepared silver carbonate and water, and the compounds are separated by means of absolute alcohol, in which, at ordinary temperatures, choline hydrochloride is readily soluble, whilst betaïne hydrochloride scarcely dissolves.

The bases were identified by their own properties and by those of their aurochlorides and platinochlorides.

Betaïne platinochloride is deposited in anhydrous needles and also in tabular crystals containing $3H_2O$, instead of 4 mols. as stated by Liebreich. The seeds contained about 0·5 per cent. of betaïne and 0·1 per cent. of choline. J. B. T.

Soil and Nitrification. By P. P. Dehérain (*Compt. rend.*, **116**, 1091—1097).—Drainage from unmanured land, and land which was manured with 60,000 kilos. of farmyard manure per hectare, contained the following amounts of nitric nitrogen (kilos. per hectare):—

	Spring.	Summer.	Autumn.	Winter.
Unmanured	28·87	15·21	31·69	15·17
Manured.....	52·21	24·79	42·89	19·44

In practical agriculture, only a portion of this nitrogen is utilised; wheat and oats take up the nitrates formed in the spring, root crops that formed in the summer; the nitrates formed in the autumn and winter are lost.

In 1891, large vessels were filled with soil from Vauteuil (Seine-et-Marne), and the drainage from the soils collected and examined. The following amounts of nitric nitrogen were obtained per cubic metre of soil.

	No. 1.	No. 2.
24th March, 1891	584 grams	539 grams.
7th April, „	664 „	466 „

Other soils examined in 1892 gave 884 grams and 440 grams of nitric nitrogen per cubic metre in July, and 250 and 285 grams six weeks later. It was found that soils give much greater amounts of nitrates when fresh than when kept for some time; thus soil from Wardrecques gave 116 grams of nitric nitrogen in 1890, and only 33 grams in 1891; whilst soil from Blaringhem gave 108 (in 1890) and 39 grams (in 1891). The effect of stirring on the production of nitrates was next studied. Whilst 100 grams of soil which was not touched gave only 2 milligrams of nitric nitrogen, similar soil kept stirred for the same time (1st November to 15th December) gave amounts varying from 39 to 71 milligrams. The soils yielded drainage in February and March which contained per cubic metre of drainage water the following amounts of nitric nitrogen:—

Soil not stirred.....	18·8 grams.
Soil stirred	1340·0 „

Nitrification was thus enormously increased by stirring the soil. In order to ascertain whether the time of the year had any effect on the energy of the nitrification, fresh samples of soil were taken in different months. Soils taken in November nitrified with great energy, whilst samples of the same soil taken in January and March, and kept at a very favourable temperature, gave at the most only half as much nitric acid as the samples taken in November. The energy of the nitrifying organisms thus varies with the season.

A hectare of soil 0·09 metre deep would weigh about 1000 tons or 10,000,000 times 100 grams. Calculating the results obtained with 100 grams to a hectare of soil, the amounts of nitric nitrogen would be 440 and 710 kilos. respectively, or from four to six times as much as is required in practice.

After discussing the usual method of working the soil, the author

expresses the opinion that, with more suitable implements for the trituration of the soil, a more vigorous nitrification could be induced, analogous to that obtained in the laboratory. N. H. M.

Analytical Chemistry.

Distillation Apparatus for Analysis. By M. Müller (*Zeit. angw. Chem.*, 1893, 229—230).—When estimating nitrogen by the Kjeldahl process, it is of great importance that no fixed alkali shall find its way into the distillate. The author agrees that the apparatus now in use are trustworthy enough when the distillation proceeds quietly, but considers that when the liquid boils briskly, a source of error through spirting may be introduced.

The author connects the distilling flask, which is fitted with a doubly perforated india-rubber cork, with a pipette-like apparatus, one end of which is suitably bent and connected with the condenser. The lower end is bent twice at right angles, and connected by means of an india-rubber joint with a narrow tube which reaches nearly to the bottom of the distilling flask. At a short distance from the bottom of the 70 c.c. pipette is fixed a rectangular wide tube, which just reaches down to the top of the distilling flask and admits the ammoniacal steam. A portion of the steam keeps on condensing in the pipette, and runs back into the distilling flask, carrying with it any trace of fixed alkali which has spirted over. L. de K.

Estimation of Small Quantities of Combustible Gas mixed with Air. By H. Le Chatelier (*Ann. Chim. Phys.* [6], **29**, 289—320).—In order to assure safety in coal mines, the "fire damp" must be diluted with air by means of efficient ventilation. The air leaving the mine ought not to contain more than 0·5 per cent. by volume of "fire damp." In order to regulate this ventilation, it is necessary to know the quantity of fire damp which is evolved in a given time; and to arrive at this, the volume of the air circulating within the mine and the percentage of "fire damp" which it contains must be ascertained. The first of these determinations needs no remarks. To accomplish the second, the author describes the following method, which occupies the first section of the paper. Pure air may be rendered inflammable by adding to it 6 per cent. by volume of methane, but obviously it will be necessary to add a less quantity of methane in order to render air inflammable which already contains "fire damp." The principle of this method has already been made use of by Schaw, but he did not succeed in solving the practical difficulties of the problem. The author has obtained estimations which are accurate to 0·1 per cent. He employs a graduated glass eprouvette of special construction, in which the combustible mixture is prepared.

In the second section of the paper, another method of estimating

the percentage of combustible gas mixed with air is described, which depends on the combustion of the mixture in contact with incandescent wires. A. R. L.

Volumetric Estimation of Free Chlorine. By C. Friedheim (*Zeit. anorg. Chem.*, **4**, 145—150).—It is well known that when this estimation is carried out by adding chlorine water to sodium carbonate solution, then adding potassium iodide, and titrating the liberated iodine with thiosulphate, the obtained results are too low. This is not through the formation of iodite or iodate, because, although more iodine may be liberated by acidifying the mixture after finishing the first titration, the total amount liberated is still less than is equivalent to the chlorine taken. Accurate results are, however, obtained if the chlorine is absorbed in sodium carbonate, the solution added to another of potassium iodide containing excess of sulphuric acid, and the liberated iodine then titrated. The real reason of the discrepancy above noticed is that, in alkaline solution, the thiosulphate is in part oxidised to sulphate, instead of exclusively to tetrathionate. C. F. B.

Specific Gravity of Solutions of Bleaching Powder. By G. Lunge and F. Bachofen (*Zeit. angw. Chem.*, 1893, 326—328).—The authors have constructed a useful table giving the amount of available chlorine corresponding with the specific gravity of solutions of bleaching powder. The specific gravity was taken by means of a delicate hydrometer, showing a difference of 0·0005 at a temperature of 15°. The chlorine was then at once estimated by Penot's arsenic method, which was checked by Lunge's hydrogen peroxide process. When the amount of chlorine is large, the specific gravity process may be taken to be accurate within 0·05 gram of chlorine per litre; when small, within 0·02 gram. L. de K.

Estimation of Iodine in Haloïd Salts by the Action of Arsenic acid. By F. A. Gooch and P. E. Browning (*Zeit. anorg. Chem.*, **4**, 178—185).—The authors draw attention to the similarity between the method recently published by Friedheim and Meyer (this vol., ii, 183) and that originated by themselves (Abstr., 1890, 1186). They point out that Friedheim and Meyer ought to have obtained better results than they have published; the purity of their reagents is suspected, and doubt is cast on the retention of bromine and chlorine in the retort while distilling over the iodine, if these exceed the limits first laid down by the authors. A. G. B.

Estimation of Fluorine in Combustible Gases. By M. Meslans (*Bull. Soc. Chim.* [3], **9**, 109—111).—A measured volume of the gas, usually an organic fluoride, is passed into the centre of a glass flask of some 500 c.c. capacity through a glass tube terminating in a platinum one, beneath which a platinum spiral, heated by an electric current, is arranged. The flask contains a known volume of standard potash, and has been previously filled with oxygen under slightly diminished pressure. The gas burns on meeting the incandescent spiral, and the fluorine contained in it forms hydrogen fluoride,

which is at once absorbed by the potash solution; the excess of the latter is determined by titration, or lime water may be used instead of potash, and the resulting calcium fluoride weighed. C. F. B.

Estimation of Phosphorus in Soils. By A. CARNOT (*Bull. Soc Chim.* [3], **9**, 343—346).—10 grams of sifted soil, dried at 100°, is charred if much organic matter be present, moistened first with water and then with nitric acid until there is no more effervescence, and finally digested with 10 c.c. of nitric acid for two hours at about 100° with frequent stirring and addition of fresh acid to replace that which has been evaporated. The mass is washed on to a filter with hot water, the filtrate evaporated to a volume of 50 c.c., and 5 c.c. of concentrated nitric acid, together with 0·5 gram of chromic acid crystals, are added; the dish is then covered with a clock glass, and its contents heated to boiling for half an hour. 5 grams of ammonium nitrate and 50 c.c. of ammonium molybdate solution are next added, and the liquid kept at a temperature of about 100° for an hour, at the end of which time the phosphoric acid will have been completely precipitated. The ammonium molybdate solution is prepared by dissolving 150 grams of the crystallised salt in a litre of water, and pouring the solution into a litre of nitric acid of sp. gr. 1·20; after the liquid has been kept at 60° for three or four days, it is decanted from the deposit. The precipitate is washed by decantation twice with water containing one-fifth of its volume of ammonium molybdate solution, the washings being passed through a small filter, and dissolved in 30 c.c. of ammonia diluted with an equal bulk of warm water. The solution, which, together with the washings, measures 80 c.c., is now neutralised with nitric acid, care being taken that the temperature does not rise above 40°. When the yellow precipitate ceases to redissolve on agitating the liquid, a mixture of 3 c.c. of pure nitric acid, 4 or 5 c.c. of water, and the same quantity of molybdate solution is added. After the precipitate has settled for two hours, it is filtered through a weighed filter, washed first with water containing 1 per cent. of nitric acid and finally with a little pure water, dried at 100°, and weighed. The weight of the precipitate multiplied by the factor 0·0373 gives the quantity of phosphoric acid contained in the 10 grams of soil.

The author has convinced himself that the second precipitation of the yellow precipitate renders unnecessary the tedious process, generally adopted, of rendering the silica of the soil insoluble; the introduction of sodium silicate into the solution did not appreciably alter the percentage of phosphoric acid found. A. G. B.

Estimation of Phosphoric acid as Magnesium Pyrophosphate. By H. NEUBAUER (*Zeit. anorg. Chem.*, **4**, 251—266; compare this vol., ii, 236).—Ammonium magnesium phosphate varies in composition with the conditions under which it is precipitated, and three cases may be recognised:—(1) When the precipitate is formed in a neutral or ammoniacal solution, which does not contain an excess of magnesium salt. In this case the ammonium salts present so affect the precipitate that it contains less magnesia than is required for the

normal salt; this entails a loss of phosphoric acid when the precipitate is ignited. (2) When the precipitate is thrown down by the addition of an excess of magnesium salt, no excess of ammonia being present. In this case, normal ammonium magnesium phosphate is produced, and the analytical results are correct. (3) When the precipitate is thrown down by an excess of magnesium salt in the presence of an excess of ammonia. In this case the precipitate contains more magnesia than is required for the normal salt, and the analytical results are too high.

The author recommends the following method:—The separation of the ammonium phosphomolybdate is effected as usual, care being taken that precipitation of free molybdic acid is avoided. The precipitate is dissolved in 100 c.c. of cold 2½ per cent. ammonia solution, and the phosphoric acid precipitated by dropping in, with constant stirring, as many c.c. of magnesia mixture (55 grams of crystallised magnesium chloride and 70 grams of ammonium chloride dissolved in 1 litre of 2½ per cent. ammonia solution) as there are centigrams of phosphoric anhydride present. At least one minute should be occupied in adding 10 c.c. of the magnesia mixture. After the precipitation, the liquid is vigorously stirred, and left for at least three hours, when the precipitate is collected and washed with 2½ per cent. ammonia water until the chlorine reaction has disappeared. The dried filter is transferred, with the precipitate, to a platinum crucible, and burnt, the temperature being gradually raised to a medium red heat until the precipitate is quite white. Ignition over the blowpipe until the weight is constant is necessary. To the weight of the magnesium pyrophosphate must be added a correction for the loss on ignition; a table is given which shows the milligrams to be added to quantities of pyrophosphate from 0·01 to 0·35 gram; in the last case, the correction amounts to 11 milligrams. A. G. B.

Volumetric Estimation of Phosphoric acid. By A. F. Holleman (*Rec. Trav. Chim.*, **12**, 1—11).—Various volumetric methods hitherto employed are enumerated, discussed, and rejected as unsatisfactory. The following method is then proposed:—In a flask of 200 c.c. capacity are placed 50 c.c. of the liquid to be analysed (which should not contain more than 0·2 gram of phosphoric acid), 10 c.c. of a normal solution of sodium acetate, and then a slight excess of decinormal silver nitrate (4·5 c.c. for every 0·01 gram P_2O_5 supposed to be present). The solution is then neutralised with N/10 soda, the amount required having been determined by previously titrating 10 c.c. of the liquid to be analysed, using phenolphthaleïn as indicator; five times this amount is, of course, taken, or, better, five times less ½ c.c. The phosphoric acid is, in the presence of sodium acetate, completely precipitated as silver phosphate, and the excess of silver is determined by diluting the mixture to 200 c.c., filtering, and titrating 100 c.c. of the filtrate with thiocyanate according to Volhard's method. The results agree well with those obtained gravimetrically. Sulphuric and nitric acids may be present, but not hydrochloric. Alkali and alkaline-earth metals may be present, but not heavy metals. If iron and aluminium are present, 100 c.c. is

precipitated with 20 c.c. of normal sodium acetate, the phosphoric acid is determined in 50 c.c. of the filtrate, and the precipitate of iron and aluminium phosphates is ignited and weighed, and its weight, multiplied by 0·45/2, is added to the weight of phosphoric anhydride found volumetrically. If ammonia is present, it must be removed by boiling with soda, as, otherwise it affects the titration with phenolphthaleïn. C. F. B.

Estimation of Boric acid. By A. K. Reischle (*Zeit., anorg. Chem.*, **4**, 111—116).—Several of the methods hitherto used have been examined and found defective; the following is recommended. The substance is slowly warmed in a platinum crucible with six times its weight of resublimed ammonium fluoride, when ammonium borofluoride volatilises. After cooling, the residue is treated with strong sulphuric acid, evaporated to dryness, and ignited. From the difference in weight of the sulphate found and borate taken, the amount of boric acid originally present may be calculated. The results are accurate; with borax they varied from 99·6 to 99·9 (in one case 99·3) per cent. of the theoretical; in the case of a mixture of freshly-ignited lime with boric acid, from 100·3 to 100·5 (in one case 98·5) per cent. C. F. B.

Analysis of Silicates by Deville's Method. By F. Glinka (*J. Russ. Chem. Soc.*, **24**, 456—458).—The author uses Deville's method of silicate analysis in preference to those usually employed, as it admits of the determination of silica, alumina, and alkalis in one portion of material; he considers it specially applicable to soda felspars. A weighed quantity of powdered albite is mixed with the same weight of pure powdered calcium carbonate in a small platinum crucible, which is carefully heated first over a Müncke burner, and finally over the blowpipe, the heat being very gradually applied, until at last the whole mass has fused to a homogeneous liquid, which is kept fused for 10—15 minutes. On cooling, the melt can be easily decomposed by means of nitric or hydrochloric acid. The analysis is then conducted in the ordinary manner.

The calcium carbonate employed was prepared by dissolving marble in nitric acid, evaporating to drive off the acid, dissolving in water, and precipitating with ammonium carbonate. The filtered and carefully-washed precipitate was dried first at the ordinary temperature, and finally at 130—150°. J. W.

Estimation of Carbon in Iron and Steel. By O. Pettersson and A. Smett (*Zeit. anorg. Chem.*, **4**, 305—308).—This method has already been described (Abstr., 1890, 1027); it is now proposed to absorb the sulphurous anhydride by solid chromic acid, and to pass the gas over red-hot copper oxide before it is absorbed by the baryta water, in order to burn any hydrocarbons. A convenient form of apparatus is figured. A. G. B.

Estimation of Carbon in Steel. By R. Lorenz (*Zeit. angw. Chem.*, 1893, 313—324, 395—397, 411—414).—The author criticises the various processes in use for the estimation of carbon in steel,

and comes to the conclusion that when accurate results are wanted, the carbon should be estimated by direct combustion.

This process is not new, having been, in fact, employed and recommended by Regnault. But, after investigation by many eminent chemists, it has been practically abandoned, as the results obtained were generally below the truth.

The author has now revived the process. The finely divided sample is mixed in a porcelain boat with fused and powdered lead chromate. The boat is placed inside a long porcelain tube, which is now put in a specially constructed furnace, previously described by the author, a modification of the well-known Glaser furnace, by means of which a powerful white heat can be obtained.

The sample is burnt in a current of pure and dry oxygen, which then passes over red-hot copper oxide, contained in a second porcelain boat, heated in an ordinary gas combustion furnace. The carbonic anhydride formed by the combustion of the steel is passed through a series of soda-lime absorption tubes, and finally weighed.

L. DE K.

Volumetric Estimation of Copper, Iron, and Antimony, and of Zinc in Zinc Powder. By F. JEAN (*Bull. Soc. Chim.* [3], 256—258).—The method described for the estimation of copper is that devised by Weil in 1869, which consists in titrating a boiling solution of cupric salt, in the presence of a large excess of hydrochloric acid, with stannous chloride. Stannous chloride (4·5—5 grams) is dissolved in water (100 grams), and hydrochloric acid (30 grams) added. The titration is conducted in a flask of white glass, in the presence of 0·25 gram of hydrochloric acid; the stannous chloride is added drop by drop to the boiling solution until the colour is quite destroyed. Ferric chloride may be titrated in like manner. To estimate iron and copper in the presence of each other, the volume of stannous chloride solution necessary for the reduction of the two salts is first ascertained, the copper is then precipitated by boiling the solution with granulated zinc, and the iron titrated alone. Antimony perchloride may also be titrated with stannous chloride. To estimate antimony and copper in a solution containing both metals, the two are first titrated together, the copper is then reoxidised by a current of air or by potassium permanganate, and the solution again titrated.

When zinc powder is treated with an excess of a neutral solution of copper of known titre, an equivalent amount of copper is precipitated, and by titrating the excess with stannous chloride solution, the percentage of zinc may be estimated. Test analyses are not given.

A. R. L.

Separation of Metals in Alkaline Solution by Hydrogen Peroxide. By P. JANNASCH (*Ber.*, **26**, 1496—1499; compare Abstr., 1892, 537).—*Separation of Lead from Silver.*—About 0·5 gram of each of the nitrates is dissolved in water (50 c.c.), the solution acidified with concentrated nitric acid (2 c.c.), and treated at ordinary temperatures with a mixture consisting of 15—20 c.c. of hydrogen peroxide (2 per cent.) and 15 c.c. of concentrated ammonia; saturated solution

of ammonium carbonate (5 c.c.) is then added, the brownish-yellow lead oxide is separated, washed with dilute ammonia, then with water, and ignited in a platinum crucible which is placed in an air-bath, the residue is treated with nitric acid, the nitrate dissolved in water, the solution evaporated to dryness, and the residue weighed after fusion.

The filtrate containing the silver is evaporated until free from ammonia, acidified with nitric acid, and the silver determined in the usual manner.

The lead may also be precipitated with hydrogen peroxide, in presence of ammonium sulphate, in sulphuric acid solution, but greater attention requires to be paid to the strength of the various reagents.

Separation of Silver from Bismuth.—This is effected in a similar manner to the preceding; the addition of ammonium carbonate is unnecessary.

The numerical results show that a considerable degree of accuracy can be attained by this method of separation. J. B. T.

Separation of Lead from Silver in Ammoniacal Solution by means of Chromic acid. By P. JANNASCH (*Ber.*, **26**, 1500; compare preceding abstract).—The mixed nitrates (0·5—0·6 gram of each) are dissolved in water (100 c.c.), dilute nitric acid (2 c.c.) is added, and the liquid boiled in a porcelain dish; boiling 10 per cent. solution of potassium dichromate (6 c.c.) is then added, and afterwards dilute (1 : 3) ammonia (15 c.c.); the precipitate is heated on the water-bath for 15—20 minutes, allowed to cool, filtered, and washed, first with dilute ammonia, and finally with water. The silver is determined in the filtrate by the ordinary method.

The accuracy of the method is shown by numerical results.

J. B. T.

Analysis of Impure Galena, and a Method of estimating Copper and Zinc. By F. JEAN (*Bull. Soc. Chim.* [3], **9**, 253—258).—25—30 grams of the mineral, finely pulverised and passed through a silk sieve, are boiled for an hour in a porcelain capsule with a concentrated solution of sodium sulphide, to which sulphur is added, the water being replaced at intervals as it evaporates. The liquid is now diluted with water, and after a while the clear solution is decanted, and the insoluble matter washed by decantation. The solution is acidified, and the precipitated sulphides of antimony and arsenic collected, dried, and weighed; when their amount is large, an aliquot portion, or when otherwise, the whole, is treated with aqua regia at a moderate temperature, and the solution filtered from sulphur, the latter being again treated with aqua regia. The united liquids are concentrated, boiled, with the addition of hydrochloric acid, until chlorine is no longer evolved, and made up with water to 100 c.c. The antimony is then estimated in 25 c.c. of the solution by titrating it with a standard solution of stannous chloride, in the presence of 10 c.c. of a solution of copper sulphate containing 0·7 gram of that salt (Weil's method). After ascertaining the relative values of the copper and stannous chloride solutions, the amount of copper used in the test is deducted from the amount (calculated as copper)

found in the test; the difference multiplied by 0·66214 gives the antimony. The arsenic is estimated in another 25 c.c. portion of the solution by precipitation as ammoniomagnesic arsenate in the presence of tartaric acid.

The mineral, deprived of antimony and arsenic, is heated to redness, in an iron scorifier, with 10 grams of ammonium nitrate; after three or four such treatments, the sulphides are transformed into oxides. The pulverised mass is then digested with hydrochloric acid, in a porcelain capsule, to dissolve the zinc and copper; a little lead also goes into solution, but the greater portion remains as oxide; the mixture is diluted with water (500 c.c.), and allowed to remain, in order that the lead chloride (and also a little silver chloride) may separate. The clear liquid is decanted, the residue washed by decantation, the whole of the liquors united, and sodium phosphate added, which precipitates the lead chloride, the manganese, magnesium, and calcium; subsequently ammonia and ammonium chloride are added. The precipitate is dried and added to the principal residue containing the remainder of the lead and silver, which is then fused in a crucible with sodium carbonate, a little borax, and 1—2 grams of flour. The metallic button of lead and silver is then weighed, and the silver estimated by cupellation.

The ammoniacal solution contains copper and zinc, the amounts of which are estimated by titration with a solution of sodium sulphide, employing paper impregnated with lead carbonate as indicator. [The titre of the sodium sulphide solution is previously ascertained by direct titration of ammoniacal solutions containing known weights of zinc and copper.] The copper is then, after acidification, precipitated in another portion of the solution as sulphide, and ammonia and ammonium carbonate added to the filtrate, in which the zinc is then estimated alone by titration with sodium sulphide. Test analyses are not given. A. R. L.

Analysis of Pigments ground in Oil. By J. B. Hannay (*Chem. News*, **67**, 268—269).—To completely extract oil from ground pigments, the author recommends using no less than 100 c.c. of fresh methylated ether for every gram of the sample. On treating ground white lead in this manner, he has always succeeded in getting a residue perfectly soluble in dilute nitric acid. The author ridicules the idea that Dutch white lead owes its superior quality to the fact that it causes a saponification of the oil. On passing hydrogen sulphide into the ethereal solution, he has never succeeded in obtaining a precipitate of lead sulphide, showing the absence of lead oleate. L. de K.

Analysis of Ground White Lead. By R. H. Harland (*Chem. News*, **67**, 301).—The author does not agree with Hannay (see preceding abstract), and states that after extracting 50 grams of Stack white lead with 5 litres of ether, the residue did not dissolve to a clear solution in nitric acid, but a distinct trace of oil separated. The ethereal solution, after its volume had been greatly reduced by distillation, gave a distinct black precipitate with hydrogen sulphide. L. de K.

Quantitative Analysis by Electrolysis. By A. CLASSEN (*Zeit. anorg. Chem.*, **3**, 404—406).—A further reply to Rüdorff (this vol., ii, 391).

Electrolytic Separation of Metals. By E. F. SMITH and J. C. SALTAR (*Zeit. anorg. Chem.*, **3**, 415—420).—*Copper from Bismuth.*—The text-books are not agreed as to the possibility of this separation in the presence of free nitric acid. The authors find that either metal alone can be completely precipitated, provided, in the case of bismuth, that the amount of nitric acid is not more than is necessary to prevent the formation of basic nitrate, otherwise part of the bismuth is deposited on the anode as peroxide. But from a solution containing both metals, the copper, although completely precipitated, is always contaminated with bismuth, and a further portion of the latter is precipitated as peroxide on the anode.

Lead from Bismuth.—Lead is completely precipitated as peroxide from a solution containing free nitric acid, but in the presence of bismuth the peroxide is invariably contaminated with that substance.

Copper from Lead and Bismuth.—Copper can be completely precipitated in a pure condition from solutions containing free nitric acid and small quantities (up to 1 per cent. of the copper) of lead and bismuth, but when larger quantities are present, the metal is contaminated, both with lead peroxide and with metallic bismuth.

JN. W.

Separation of Copper from Bismuth. By A. CLASSEN (*Zeit. anorg. Chem.*, **4**, 234—235).—The author disclaims origination of the statement in his book on electrolysis, quoted by Smith and Saltar (preceding abstract). It has long been known that copper cannot be deposited pure when bismuth is present. That bismuth cannot be separated electrolytically from lead in a nitric acid solution, nor mercury from bismuth, under similar conditions, has already been pointed out by the author (*Ber.*, **19**, 323). A. G. B.

Electrolytic Separation of Copper from Antimony. By E. F. SMITH and D. L. WALLACE (*Zeit. anorg. Chem.*, **4**, 273—274).—If antimony be converted into a higher oxide by bromine, and the solution containing it be mixed with tartaric acid, and made strongly alkaline with ammonia, no antimony will be deposited on electrolysis. This fact is applied to the separation of copper from antimony by electrolysis; the deposition of the former metal being complete under the above conditions. A. G. B.

Volumetric Estimation of Mercury. By J. LABORDE (*J. Pharm.* [5], **27**, 507—509).—This new method of estimating mercury, present in the mercur*ic* state, depends on the fact that when a solution of stannous chloride is added to a solution of a mercuric salt, the pure white colour of the mixture, due to precipitated mercurous chloride, changes to brown as soon as enough stannous chloride has been added to reduce all the mercuric to mercurous salt, a further reduction to metallic mercury then beginning. The solution is made by dissolving 8 grams of tin-foil in 100 c.c. of hydrochloric acid, and

diluting; it is standardised against a solution containing 10 grams of pure mercuric chloride per litre, 5 c.c. of a solution containing 100 grams each of ammonium acetate and acetic acid per litre being added for every 10 c.c. of the mercuric solution. In an actual estimation, free mineral acids must, if present, be neutralised with ammonia, ammonium acetate being first added. The reaction is affected only by the presence of gold or platinum salts, or of iron salts in large quantity. The method is rapid and accurate, and can be carried out in very dilute solution; it may also be used in the reverse sense to estimate stannous chloride. C. F. B.

Electrolytical Separation of Mercury from Bismuth. By E. F. Smith and J. B. Moyer (*Zeit. anorg. Chem.*, **4**, 96—99).—It is not the case, as is implied in Classen's *Quantitative Analyse durch Electrolyse*, 3rd ed., p. 147, that mercury can be separated from bismuth by electrolysis in a solution containing free nitric acid. The mercury is, it is true, completely precipitated, except when the current is small and the amount of acid large, but it is always contaminated with bismuth, as, indeed, Classen has himself stated (*Ber.*, **19**, 325), and some bismuth is also deposited on the anode. C. F. B.

Electrolytic Separations. By E. F. Smith and J. B. Moyer (*Zeit. anorg. Chem.*, **4**, 267—272; compare Smith and Saltar, *J. Anal. Chem.* **7**, 128).—*Mercury from Lead.*—Mercury, as mercuric nitrate, 0·1150 gram; lead, as nitrate, equivalent to 0·0126 gram of lead peroxide; nitric acid (sp. gr. 1·3), 30 c.c.; total volume, 175 c.c.; current, 1·8 c.c. detonating gas per minute. Mercury deposited, 0·1150 gram; lead peroxide deposited, 0·0126 gram.

Silver from Lead.—Silver, as nitrate, 0·1208 gram; lead, as nitrate, equivalent to 0·0144 gram of lead peroxide; nitric acid (sp. gr. 1·3), 15 c.c.; total volume, 200 c.c.; current, 1·8 c.c. detonating gas per minute; silver deposited, (1) 0·1023, (2) 0·1028 gram; lead peroxide deposited, (1) 0·0144, (2) 0·0145 gram.

Copper from Cadmium.—Copper, as sulphate, 0·1341 gram; cadmium, as nitrate, 0·1 gram; nitric acid (sp. gr. 1·2), 5 c.c.; total volume, 200 c.c.; current, 0·6 c.c. detonating gas per minute. Copper obtained, 0·1346 gram, containing no cadmium.

Copper from Zinc.—Metals, the same weight as for copper from cadmium; nitric acid (sp. gr. 1·3), 5 c.c.; total volume, 200 c.c.; current, 1 c.c. detonating gas per minute; copper deposited, 0·1345.

Copper from Zinc, Cobalt, and Nickel.—Metals, the same weights; nitric acid (sp. gr. 1·3), 5 c.c.; total volume, 200 c.c.; current, 0·4 c.c. detonating gas per minute. Copper deposited, 0·1339 gram.

Copper from Iron and Zinc.—Metals, the same weights; volumes, the same; current, 0·7 c.c.; copper deposited, 0·1340 gram.

Bismuth from Cadmium.—Bismuth, as nitrate, 0·0718 gram; cadmium, as nitrate, 0·1 gram; nitric acid (sp. gr. 1·1), 15 c.c.; total volume, 180 c.c.; current, 1·6 c.c.; bismuth deposited, 0·0716 gram.

Bismuth from Nickel.—Bismuth, 0·0718 gram; nickel, 0·1 gram;

nitric acid (sp. gr. 1·3), 3 c.c.; total volume, 200 c.c.; current, 0·2 c.c.; bismuth deposited, 0·0716 gram.

Bismuth from Cobalt.—Bismuth, 0·0718 gram; cobalt, 0·1 gram; nitric acid (sp. gr. 1·3), 3 c.c.; current, 0·2 c.c.; bismuth deposited, 0·0714 gram.

Bismuth from Cobalt, Nickel, and Zinc.—Bismuth, 0·0718 gram; zinc, 0·1 gram; nickel, 0·1 gram; cobalt, 0·1 gram; nitric acid (sp. gr. 1·3), 8 c.c.; total volume, 200 c.c.; current, 0·4 c.c. Bismuth deposited, 0·0718 gram. The separation is attended with greater difficulty than the separation of bismuth from any one of these three metals.

The authors conclude that nitric acid solutions are not so well adapted as those containing sulphuric acid for the electrolytic separation of bismuth from other metals (compare Abstr., 1886, 923).

A. G. B.

Estimation of Manganese Oxides by means of Hydrogen Peroxide. By A. CARNOT (*Compt. rend.*, **116**, 1295—1297).—When an oxide of manganese is mixed with hydrogen peroxide in presence of an acid, the volume of oxygen given off is double that of the oxygen present in the oxide over and above that required to form manganous oxide. The oxide is placed in a flask fitted with a cork, which carries a delivery tube and a funnel with a stop-cock. Dilute nitric acid (2 : 3) is then added, and, after evolution of carbonic anhydride has ceased, the stop-cock is closed. A measured volume of hydrogen peroxide solution is then poured into the funnel, and is allowed to run gradually into the flask, the oxygen evolved being collected over water. If the temperature and pressure remain constant during the experiment, the volume of gas collected, less the volume of the hydrogen peroxide solution added, is the volume of the oxygen.

C. H. B.

Estimation of Manganese by Oxydimetric Methods. By A. CARNOT (*Compt. rend.*, **116**, 1375—1378).—The estimation of manganese by oxydimetric methods requires that the metal shall be in a definite state of oxidation. The ordinary methods of heating the oxide or the nitrate do not give trustworthy results. If, however, the manganese is dissolved in concentrated nitric acid and potassium chlorate is added in successive small quantities to the warm liquid, manganese peroxide is precipitated, and the other metals, as a rule, remain in solution. The whole of the iron is not eliminated at the first, but a repetition of the treatment (the manganese peroxide being first dissolved in a mixture of nitric acid and hydrogen peroxide) yields a pure product.

Even better results are obtained by mixing the manganese solution with hydrogen peroxide, and then quickly adding excess of ammonia and boiling the liquid for some minutes. The product has the composition Mn_3O_{11} or $MnO,5MnO_2$. Large quantities of ammonium salts tend to prevent the formation of the peroxide, but their influence can be counteracted by the use of a larger quantity of hydrogen peroxide. Copper, zinc, nickel, and cobalt, if present, are partially precipitated in the form of manganites, but the elimination of these metals is easily secured by repeating the precipitation. With large

quantities of copper, nickel, and zinc, three precipitations usually suffice; with cobalt, five may be necessary. Iron does not affect the results of the analysis, but it may be removed, if desired, by first precipitating with nitric acid and potassium chlorate, dissolving the precipitate in dilute nitric acid and hydrogen peroxide, and then precipitating with hydrogen peroxide and ammonia.

The manganese may also be precipitated by bromine and ammonia in the cold, if care is taken that the bromine remains in contact with the almost neutral manganese solution for some time; but the method is not so convenient as that just described. The precipitate has the composition Mn_6O_{11}, and must be well washed with hot water.

C. H. B.

Estimation of Manganese in Minerals. By F. Jean (*Bull. Soc. Chim.* [3], **9**, 248—252).—Pattinson's method of estimating manganese consists in precipitating the metal as dioxide and titrating the latter with strongly acidified ferrous sulphate, and subsequently with potassium dichromate. The author prefers to employ oxalic acid and potassium permanganate. This method is to be recommended when a series of manganese estimations have to be made, but it has the inconvenience of requiring a large number of solutions, and, on this account, the author prefers the following:—The finely pulverised mineral is decomposed by hydrochloric acid, the solution evaporated to dryness, and the silica collected and weighed. The filtrate is made up with water to a volume of 100—200 c.c. 25—50 c.c. of it is precipitated by sodium carbonate, the precipitate collected, redissolved in 50 c.c. of nitric acid (sp. gr. 1·2), and the solution boiled for a quarter of an hour with potassium chlorate (6—8 grams), whereby the whole of the manganese is precipitated as dioxide. It may be weighed as Mn_3O_4, or titrated with oxalic acid and potassium permanganate.

The author has obtained good results with Guyard's method, operating in the manner described by Campredon (*Mon. Sci.*, 1892). It is specially applicable in the case of spiegel-eisen, manganese steel, and ferro-manganese. The substance is decomposed by aqua regia, the nitric acid expelled by evaporation, and hydrochloric acid added. The solution is maintained at 80°, and treated with an excess of zinc oxide or calcium carbonate, whereby, after well shaking, the iron is precipitated; it is then made up to about 500 c.c. with hot water, and titrated with potassium permanganate. Test analyses are not given.

A. R. L.

Estimation of Iron and Aluminium in Bone Black. By F. G. Wiechmann (*Chem. News*, **67**, 311—312).—The author has devised the following scheme, which offers all the advantages of the Glaser and the Stutzer methods:—5 grams of the sample is dissolved in 30 c.c. of hydrochloric and 10 c.c. of nitric acid, and made up to 500 c.c. 100 c.c. of the filtrate is put into a 250 c.c. flask, and mixed with 25 c.c. of strong sulphuric acid. After well shaking and cooling, absolute alcohol is added up to the mark. As contraction takes place, it is necessary to add, after some time, a little more alcohol. After 12 hours, the liquid is filtered off, and 100 c.c. is evaporated in a

platinum dish until the spirit is expelled. The remaining solution is washed into a beaker with 50 c.c. of water, heated to boiling and rendered alkaline with ammonia, the excess of which must now be completely expelled by boiling. After washing the precipitate thoroughly with boiling water, the filter containing it is placed in a beaker containing 150 c.c. of molybdic solution at 40°, and then kept for about 12 hours at 65°. The liquid is filtered, and the precipitate well washed with a 10 per cent. solution of ammonium nitrate. The filtrate is rendered alkaline with ammonia and boiled for a few hours, a little ammoniacal water being added from time to time. The precipitate now consists of ferric and aluminic hydroxides, but to free it from traces of molybdic acid, it must, after washing, be redissolved in hydrochloric acid and reprecipitated with ammonia. Finally, the precipitate is ignited and weighed, and reported as mixed iron and aluminium oxides. L. DE K.

Modification of the Stannous Chloride Method of titrating Iron. By R. W. MAHON (*Amer. Chem. J.*, **15**, 360).—To determine the end of the reduction in this process, the author employs a solution containing 0·05 gram of platinum, in the form of platinic chloride, and 34 grams of mercuric chloride per litre as indicator. Stannous chloride in presence of this solution reduces the whole of the ferric salt to the ferrous state, and then precipitates a dark cloud of mercurous chloride mixed with metallic mercury and platinum. The iron solution is made up to about 125 c.c., and contains 20—40 c.c. of hydrochloric acid of sp. gr. 1·20; the liquid is heated almost to the boiling point and titrated, after the addition of 15 c.c. of the indicator solution. 0·2 c.c. must be subtracted for the final reaction. Results excellent. A. H.

Analysis of Iron and Steel. By J. PARRY and J. J. MORGAN (*Chem. News*, **67**, 149—150, 161—162, 175—177, 247—248, 259—261, 295—296, 307—308).—The authors describe the most trustworthy processes in use for the estimation of the minor constituents in iron and steel, such as silicon, phosphorus, total and graphitic carbon, manganese, copper, arsenic, nickel, cobalt, chromium, aluminium; also tungsten, titanium, calcium, magnesium, and iron oxide. As regards the rarer of these substances, the authors remark that, although, no doubt, frequently occurring, they are but rarely recorded in analytical certificates, for the simple reason that they are seldom looked for.

Iron oxide (Fe_3O_4), which is always present in the samples, is best estimated by a process devised by Parry. 10 grams of the sample is dissolved at a gentle heat in 500 c.c. of a mixture of potassium dichromate and sulphuric acid (1 part of acid to 6 parts of saturated dichromate solution). When it is judged that the whole of the iron has dissolved, the solution is allowed to remain until settled, when the supernatant liquid is passed through a filter. The insoluble residue is now washed a few times with water by decantation, and afterwards digested with aqueous potash to remove the silica. The residue is now well washed on the filter, first with the alkali and then

with water, until the alkali has been completely removed. The filter is afterwards strongly ignited, and the residual ferric oxide weighed.

L. DE K.

Separation of Nickel and Cobalt by means of Nitroso-β-naphthol. By G. v. KNORRE (*Zeit. angw. Chem.*, 1893, 264—269).—The author recommends the following process for the assay of commercial nickel:—5 grams of the sample is dissolved in 50 c.c. of nitric acid of sp. gr. 1·2, in a covered beaker. When dissolved, the liquid is put into a porcelain dish, 10 c.c. of sulphuric acid is added, and the whole evaporated until sulphuric acid fumes begin to be evolved; when cold, water is added, and the mixture heated until all the nickel sulphate has dissolved. Any insoluble silicic acid is then collected, and should, after weighing, be tested as to its purity by means of hydrofluoric acid.

The filtrate is mixed with 50—100 c.c. of solution of hydrogen sulphide and warmed to assist the separation of any copper sulphide, which may then be collected, washed with solution of hydrogen sulphide, and converted into oxide by ignition. The filtrate is concentrated and, after cooling, made up to 250 c.c. 100 c.c. is pipetted off and freed from iron by the addition of ammonia. As the iron precipitate always contains nickel, it must be twice redissolved and reprecipitated. In another portion, the joint nickel and cobalt are precipitated by electrolysis. The solution is mixed with 5 grams of sodium sulphate and a large excess of ammonia (sp. gr. 0·91). The author employed 6—8 Meidinger cells, or Gülcher's thermo-column. Sodium sulphate is preferable to ammonium sulphate, as the latter forms a less soluble double compound with the nickel. After weighing, the metal is dissolved in nitric acid, evaporated with sulphuric acid, dissolved in dilute hydrochloric acid, and the cobalt precipitated by the addition of nitroso-β-naphthol. Formerly the author adopted the plan of mixing the dried precipitate with oxalic acid before ignition, as the compound is slightly explosive; but he has found that the conversion of the salt into oxide (Co_3O_4) may be effected, without risk, by introducing the moist filter containing it straight into a platinum crucible, which is then at once heated to redness. Operating in this manner, it is also easier to get rid of the last traces of carbonaceous matter. The test analyses given are highly satisfactory. The process is not only serviceable for the precipitation of cobalt in presence of nickel, but also for the separation of iron from aluminium and phosphoric acid, iron from copper or manganese, &c.

L. DE K.

Quantitative Separations in presence of Hydroxylamine. By P. JANNASCH and J. MAI (*Ber.*, **26**, 1786—1787).—The addition of a certain quantity of hydroxylamine to the solution of a salt before precipitating the metal with ammonia has frequently a remarkable influence on the result. In some cases, the properties of the precipitate are considerably altered, in others no precipitate is formed, whilst in others precipitates are obtained which are not produced when ammonia alone is used. An example of the first effect is found in the case of chromium, which is precipitated from solutions of its salts by ammonia in presence of hydroxylamine as a violet-red pre-

cipitate; the latter can be collected and washed with much greater ease than the green precipitate obtained by the use of ammonia alone.

Further investigation of the effect of hydroxylamine in quantitative separations is now in progress. H. G. C.

Assay of Tin Ore. By T. Moore (*Chem. News*, **67**, 267—268).—Half a gram of the ore mixed with 5 or 6 grams of powdered zinc (prepared by triturating melted zinc in a hot iron mortar and separating coarser particles by sifting) is placed on, and covered with, a layer of the zinc powder in a porcelain crucible, a piece of charcoal is put on the top, and the covered crucible heated in a muffle until the volatilisation of zinc nearly ceases. When cool, the charcoal is removed, and the crucible and its contents treated with hydrochloric acid. The filtered solution is concentrated, made to contain a quarter of its volume of hydrochloric acid, heated nearly to boiling for 15 minutes with 5 or 6 grams of granulated lead, the solution poured into a measured excess of ferric chloride solution, and the unreduced iron titrated with cuprous chloride, using potassium thiocyanate as an indicator; from the amount of iron reduced the amount of tin is found. The heating with lead reduces stannic to stannous compounds without the production of metallic tin. D. A. L.

Method for the Simultaneous Estimation of Carbon and Nitrogen in Organic Compounds. By F. Klingemann (*Annalen*, **275**, 92—102).—The method is that of Frankland and Armstrong (this Journal, **21**, 109). The substance (0·1—0·15 at most) is burnt with copper oxide in a tube which is exhausted before and after the experiment with a Sprengel pump. The total volume of the gaseous products is measured, and subsequently that of the residual gas after the absorption of the carbonic anhydride. One experiment takes about 2¼ hours. A. R. L.

Detection of Adulteration in Wines. By Marouby (*Bull. Soc. Chim.* [3], **9**, 13—16).—Test papers are prepared by soaking blotting-paper in the necessary reagents and drying. From the appearance of the spots caused by drops of wine on the various papers, it is possible to detect many sophistications, as is evidenced by a table given of the appearances of the centres, intermediate and exterior zones of the spots given by wines to which various foreign substances have been added. Foreign colouring matters generally show their effect more in the central and intermediate portions of the spots, the exterior zone being characteristic of the natural colouring matters of the wine. W. T.

Estimation of the Dry Residue from Wine. By J. A. Muller (*Bull. Soc. Chim.* [3], **9**, 6—10).—The author describes a method of obtaining the dry residue by evaporation at 100° in a current of dry carbonic anhydride. From a series of experiments, the rates of desiccation for wines containing varying quantities of glycerol are deduced; hence *the absolute residue at* 100° may be calculated by subtracting from the residue, after 12 hours desiccation, a quantity depending on the percentage of glycerol present and the quantity of

wine taken for evaporation, provided that the residue is not much more than 0·1 gram, and the desiccation is carried on exactly in accordance with the prescribed method.

When the dry residue is obtained by means of the vacuum desiccator, the loss of glycerol at 15° may be neglected, but a correction should be applied for loss near 30°. W. T.

Identification and Estimation of the Lactoses in different Milks. By G. Denigès (*J. Pharm.* [5], **27**, 413—417).—Milk of woman, ass, mare, cow, goat, sheep, or bitch yields in each case the same crystallised lactose when the whey is evaporated. The whey itself possesses the same reducing power as a solution of lactose of the same strength, but not the same rotatory power, except after hydrolysis; it behaves as if it contained, in addition to lactose, a substance which does not reduce Fehling's solution, but which is, in the case of the woman and bitch, dextrorotatory; in the case of the ass and mare, lævorotatory, but in all cases loses its optical activity when hydrolysed with dilute acid at 106—110°.

In the estimation of lactose in milk, it is thus best to make use of the reducing power, rather than the optical activity. In a 100 c.c. flask are placed 10 c.c. of the milk, 2·5 c.c. of a 5 per cent. solution of sodium metaphosphate, and 60—70 c.c. of water; the mixture is shaken, 0·5 c.c. of hydrochloric acid is added, and the whole is made up to 100 c.c., shaken, and filtered. The reducing power of the whey thus obtained is determined by means of Fehling's solution, previously standardised against a solution of pure lactose of known strength.

C. F. B.

Polarimetric Examination of Gums. By Guichard (*Bull. Soc. Chim.* [3], **9**, 19—20).—The author finds several samples of gums, among a number examined, to be dextrorotatory, notwithstanding the assertion of Béchamp that there are no dextrorotatory gums. Commercial acetic acid dissolves the greater part of the dextrorotatory samples, but simply converts the lævorotatory gums into opaque white substances without change of form. The materials examined consist of mixtures of gums of different rotatory powers.

W. T.

Note.—The authur appears to be unacquainted with O'Sullivan's "Researches on Gedda Gums," Trans., 1891, 1029.—[Editors.]

Detection of Hydrocyanic acid. By S. Lopes (*J. Pharm.* [5], **27**, 550—553; from *Revista d. Cursos d. Faculd. d. Med., Rio de Janeiro*).—Some of the observations in this paper have been recently published by Autenrieth (this vol., ii, 393). It is suggested that mercuric cyanide should be looked for after testing for alkaline cyanides; the liquid is acidified with tartaric acid, ammonium chloride is added in excess, and the mixture is distilled; a double chloride of mercury and ammonium is formed, and hydrogen cyanide distils over with the steam. To test for poisonous cyanides in the presence of non-poisonous ones, such as potassium ferrocyanide, the substance is first heated at 100° with milk of lime, in order to decompose ammonium salts, which, if present, might form volatile ammonium cyanide by

reacting with the ferrocyanide; when all the ammonia has been driven off the solution is filtered, and tested as described by Autenrieth.

C. F. B.

Estimation of Thyocyanic, Hydrocyanic, and Hydrochloric acids. By P. L. JUMEAU (*Bull. Soc. Chim.* [3], **9**, 346—351).—Thiocyanates can be titrated with accuracy in the presence of hydrochloric or sulphuric acid by a solution of potassium permanganate, standardised by a solution of ammonium thiocyanate, itself valued by titration with silver nitrate in the usual manner. All the sulphur is converted into sulphuric acid, hydrocyanic acid being liberated; the permanency of the permanganate in the solution marks the end of the titration. If sulphates are to be determined in the liquid, they may be precipitated by barium chloride, after the titration, and the amount of barium sulphate corresponding with the thiocyanate deducted from the weight of the precipitate. If hydrochloric or hydrocyanic acid has to be estimated in a liquid as well as thiocyanic acid, one part of the solution may be precipitated with silver nitrate and the precipitate weighed, whilst the thiocyanic acid is determined in another portion by the method indicated. Or the silver precipitate may be dissolved in hot ammonia, the silver precipitated by hydrochloric acid, and the thiocyanic acid determined by titration in the filtrate. Should thiocyanic, hydrocyanic, and hydrochloric acids have to be all estimated in the same solution, the silver precipitate from one portion of it is treated as described above, in order to estimate the thiocyanic acid. The silver precipitate from another portion is treated by the Kjeldahl process, Nordhausen sulphuric acid and metallic mercury being used in place of the ordinary strong sulphuric acid and mercuric oxide; by this means the nitrogen of the cyanide and thiocyanate is estimated as ammonia; as the thiocyanate has been already estimated, the cyanide may be calculated; the weight of the chloride in the silver precipitate is determined by difference. The hydrochloric acid may also be estimated directly by oxidising the thiocyanic acid in the original solution by potassium permanganate, in the presence of sulphuric acid, expelling the hydrocyanic acid by ebullition, preferably in the presence of zinc, and precipitating the hydrochloric acid with silver nitrate.

A. G. B.

Detection of Free Salicylic acid in Salicylaldehyde and Methylsalicylic acid. By A. SCHNEEGANS and J. E. GEROCK (*Zeit. anal. Chem.*, **32**, 363; from *Pharm. Centralhalle*, **33**, 40).—The violet colour produced by ferric salts in solutions of salicylaldehyde and methylsalicylic acid disappears on the addition of ether, chloroform, amyl alcohol, ethylic acetate, carbon bisulphide, light petroleum, paraffin oil, benzene, toluene, or xylene, whilst that produced by salicylic acid remains. To detect the free acid in artificial wintergreen oil, the substance is shaken with 500 parts of water, and to 100 c.c. of the liquid is added 1 c.c. of a highly-dilute ferric chloride solution. If, on the addition of 5 c.c. of chloroform, the violet colour disappears, salicylic acid is absent, but in presence of 0·02 milligram, the colour will still remain visible when seen against a white background.

M. J. S.

Analysis of Tobacco. By V. Vedrödi (*Zeit. anal. Chem.*, **32**, 277—296).—The author has submitted to an experimental study each step in the methods of Kosutány and Kissling respectively for the estimation of nicotine.

Kosutány's method consists in freeing the tobacco from ammonia by mixing with lime and exposing over acid, then washing out the free nicotine with cold water, transferring it from the watery extract to light petroleum by shaking, then removing from the petroleum solution by shaking with N/10 sulphuric acid, and titrating the excess of acid. In Kissling's method, the tobacco is mixed with weak alcoholic soda and extracted in a Soxhlet's apparatus with ether; the ether is distilled off, and the residue, mixed with strong soda solution, is distilled with steam, when the nicotine passes over and is titrated in the distillate.

The chief source of error in Kosutány's method it that the petroleum does not completely abstract the nicotine from its aqueous solution. The results obtained by Kissling's method are, on the other hand, too high, unless care be taken to get rid of ammonia completely before exhausting with ether, since the ammonia is but partially removed during the evaporation of the ether, and consequently accompanies the nicotine in the subsequent distillation with steam. Moreover, certain of the nitrogenous constituents of the tobacco are dissolved by the soda, and during the distillation yield ammonia.

M. J. S.

Detection of "Saccharin" in Beer. By F. Gantter (*Zeit. anal. Chem.*, **32**, 309—312).—The author confirms Börnstein's statement that Remsen's reaction can be employed for the detection of "saccharin" in spite of the fact that resorcinol, when heated alone with sulphuric acid, yields a trifling green fluorescence. The fluorescence produced by "saccharin" is so intense that it is visible with a degree of dilution which conceals that produced by resorcinol (Abstr., 1888, 760; and 1889,449). The test cannot, however, be applied directly to an ethereal extract of beer residue, since this extract contains a substance seemingly a resin, which gives the green fluorescence with as great intensity as "saccharin" itself. Other methods of detection, such as fusion with alkali carbonate and nitrate, and examination for sulphates, and the salicylic acid reaction, are useless, on account of the small quantity of the "saccharin" to be tested for. The following method, however, seems trustworthy:—Half a litre of beer is evaporated to a syrup and, after the addition of a few drops of hydrochloric acid, is shaken in a stoppered bottle with 200 c.c. of 95 per cent. alcohol. The clear solution decanted from the precipitate is evaporated and the residue is shaken with ether. The ethereal extract is evaporated and the residue boiled with water. The aqueous solution when evaporated leaves the "saccharin" in a sufficiently pure condition to allow of its recognition by its intensely sweet, characteristic taste, this taste never being observed in the residue from pure beer.

M. J. S.

General and Physical Chemistry.

Refractive Powers for a Ray of Infinite Wave-length. By R. Nasini (*Gazzetta*, **23**, i, 347—353).—The author gives a summary and critique of recent work on refraction constants calculated for the ray A of infinite wave-length. W. J. P.

Specific Inductive Capacities and Refraction Constants. By S. Pagliani (*Gazzetta*, **23**, i, 537—552).—Maxwell has shown that the specific inductive capacity, K, and the refractive index for a ray of infinite wave-length, μ_∞, of any substance are in the relation $K = \mu^2_\infty$; if, however, the electrical resistance is infinite, a condition which holds approximately for organic compounds, it follows, from the electro-magnetic theory of light, that the refractive index is independent of the wave-length; the dispersion may hence be disregarded. Joubin has enunciated a connection between the molecular weight, M, and the refractive index, μ, of a substance, which may be resolved into the following expression,

$$\mu - 1 = C\sqrt{\frac{M}{N}},$$

where N is the number of atoms in the molecule and C is a constant. Now, taking Gladstone's refraction formula $\frac{\mu - 1}{d}$ and substituting this value in the equation for the specific inductive capacity given above, Joubin's expression becomes

$$\frac{K - 1}{K}\sqrt{\frac{N}{M}} = C_1 \quad \ldots\ldots\ldots\ldots \quad (1).$$

Similarly, using Ketteler's refraction formula $\frac{\mu^2 - 1}{\mu^2 + x} \cdot \frac{1}{d}$, and putting $x = 0$, the expression

$$\frac{K - 1}{K} \cdot \frac{N}{U} = C_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (2),$$

is obtained, in which U is the molecular volume.

The values of C_2, calculated for a long series of organic substances of different types, are more concordant than those of C_1, and both are more constant than the values of C_3, calculated by Landolt and Jahn from the equation

$$\frac{K - 1}{d(K + 2)} = C_3 \quad \ldots\ldots\ldots\ldots\ldots \quad (3).$$

The agreement of the values C_2 for homologous series is very close. By transposing equation 2, so as to obtain an expression for K, it is seen that, in a homologous series, K and M should change in the same sense; owing probably to the small differences between the values of

K and the experimental errors incurred in its determination, several exceptions are to be noted amongst the hydrocarbons.

If K is eliminated from equations 1, 2, and 3, expressions containing only μ_∞, M, N, U, and a constant may be readily obtained; on calculating the constants from these, it is found that the expressions derived from equations 1 and 2 give more concordant results than that from equation 3. W. J. P.

Electromotive Force in Electrolytic Analysis. By H. Freudenberg (*Zeit. physikal. Chem.*, **12**, 97—124).—It has been shown that different values of the electromotive force are necessary to electrolytically decompose aqueous solutions of different salts. In some cases, the electrolytic separation of two metals from a mixed solution of their salts may be effected by choosing an electromotive force just sufficient to decompose one salt, but insufficient to decompose the other. The author has made a large number of experiments on this subject, and has succeeded in effecting the separation, in acid solution, of various metals which show normal decomposition values of the electromotive force. Thus, silver may be separated from arsenic and bismuth; mercury from copper, bismuth, and arsenic; and, finally, copper and bismuth from cadmium and arsenic. Solutions with abnormal decomposition values were also investigated, without practical result in the case of the oxalates, phosphates, and ammonium double salts. Cyanides and sulpho-salts, however, often give methods of separation. For example, silver may be separated from antimony, and mercury from copper and cadmium in potassium cyanide solution, and mercury may be separated from antimony and arsenic in ammoniacal solution. J. W.

Influence of Boric acid on the Electrical Conductivity of Aqueous Solutions of Organic Acids. By G. Magnanini (*Gazzetta*, **23**, i, 197—251; compare Abstr., 1892, 256, 1625).—The author confirms his previous conclusions with regard to the influence of boric acid on the electrical conductivity of organic acids, and has further investigated the change in electrical conductivity produced by adding boric acid to solutions of β-hydroxypropionic, hydroxybutyric, α-hydroxyvaleric, trichlorolactic, levulinic, malic, hydrochelidinic, cineolic, pyromucic, isodehydracetic, hydroxydehydracetic, mesoxalic, tartronic, mucic, pyrrolinecarboxylic, acetylpyrrolinecarboxylic, *n*-methyl-α-pyrrolineglyoxylic, phenylpyrrodiazolic, meconic, trichlorodiketopentamethylenehydroxycarboxylic, meta- and para-hydroxybenzoic, ortho- and para-nitrosalicylic, protocatechuic, ortho-, meta-, and para-cresotinic, orthocoumaric, hippuric, caffeïc, cuminolcarboxylic, paraxylenolcarboxylic, benzylcresotinic, β-resorcilic, pyrogallolcarboxylic, tropic, vanillic, guaicolcarboxylic, opianic, diphenylglycollic, apionylketonic, quinic, and parahydroxyquinolineorthocarboxylic acids. The electrical conductivity of acids which do not contain hydroxyl in addition to a carboxyl group is never increased by adding boric acid to their aqueous solutions. Hydroxy-acids which contain the hydroxyl group in the α-position relatively to the carboxyl, whether open or closed chain compounds, always undergo an increase in

electrical conductivity on the addition of boric acid to their aqueous solutions; this rule seems to be obeyed independently of the other groups present in the molecule, and holds whether the hydroxyl group is attached to a primary, secondary, or tertiary carbon atom. In general, no augmentation in electrical conductivity is observed with acids containing an hydroxyl group in any but the α-position to the carboxyl; the reverse is true, however, with gallic and protocatechuic acids. W. J. P.

Constitution of Metalamine Salts. By A. Werner and A. Miolati (*Zeit. physikal. Chem.*, **12**, 35—55).—The molecular conductivity of equivalent solutions of luteocobaltic bromide, $Co(NH_3)_6Br_3$, roseocobaltic bromide, $Co(NH_3)_5(H_2O)Br_3$, and tetramineroseocobaltic bromide, $Co(NH_3)_4(H_2O)_2Br_3$, varies very slightly (from 442 to 417 for μ_{2000}), so that the substitution of water for ammonia in the salts has no marked direct effect on their basic properties. The molecular conductivities of bromopurpureocobaltic bromide, $[CoBr(NH_3)_5]Br_2$, and of xanthocobaltic bromide, $[Co(NO_2)(NH_3)_5]Br_2$, are not much greater than half those of the luteo- and roseo-salts. When bromotetraminepurpureocobaltic bromide, $[Co(NH_3)_4(H_2O)Br]Br_2$, is dissolved in water, the violet solution changes gradually into pink, the conductivity at the same time increasing. This is due to the gradual conversion of the salt into tetramineroseocobaltic bromide by a process of hydration. Other examples of similar changes were observed.

Hexaminecobaltic nitrite, $Co(NH_3)_3(NO_2)_3$, and platosemidiamine chloride are practically non-electrolytes; platosamine chloride conducts slightly. In the case of many of the platinum compounds, the conductivity rises from a very small amount to considerable proportions on standing.

Double salts, such as Erdmann's compound, $[Co(NH_3)_2(NO_2)_4]K$, give numbers for the conductivity which correspond with the assumption of a dissociation into two ions.

The author's results, in general, confirm the conclusions arrived at, on purely chemical grounds, as to the distribution of the positive and negative groups with regard to the metallic atom in the molecule.

J. W.

Electrical Furnace. By Saladin (*Bull. Soc. Chim.* [3], **9**, 133—136).—The principle of this apparatus is the same as that of the electrical cautery. A platinum spiral, rendered incandescent by means of a current of electricity, is placed in a vessel of refractory material, and the whole enclosed in a cast-steel case. A side opening in the case communicates with a pump and manometer, and admits of the pressure being increased to 1000 atmospheres; the range of temperature is 1500—1800°, and is measured by a platinum-rhodium couple. Details of the construction of the furnace are given in the original paper. J. B. T.

Fusion and Volatilisation of Metals and Oxides in the Electric Arc. By H. Moissan (*Compt. rend.*, **116**, 1429—1434).—In order to condense and collect the substances that sublime, a copper U-tube, through which a rapid current of cold water is continually.

passing, is introduced into the electric furnace immediately above the crucible containing the substance under investigation. Asbestos cardboard placed above the opening through which the U-tube is introduced serves also to condense some of the vapour.

When magnesium pyrophosphate is submitted for five minutes to the action of the arc formed by a current of 300 ampères and 65 volts, a sublimate of magnesium oxide and ordinary phosphorus is obtained. Asbestos, with 300 ampères and 75 volts, almost completely volatilises in a few minutes, and leaves only a small residue of the fused silicate, together with a small globule of magnesium silicide.

Copper, with 350 ampères and 70 volts, volatilises rapidly, and condenses in globules. The vapour forms cupric oxide in contact with air. Silver readily enters into ebullition, and distils more easily than zirconia or silica. It condenses in fused globules, a grey, amorphous powder, and arborescent fragments. Platinum melts almost immediately, and very soon begins to volatilise, condensing in brilliant globules and also in the form of a powder. Aluminium, with 250 ampères and 70 volts, likewise volatilises, and condenses in small spherules. Tin, with 380 ampères and 80 volts, volatilises readily, and condenses in small globules and in fibrous masses. Gold, with 360 ampères and 70 volts, volatilises to a considerable extent, even in six minutes, and condenses in small spheres. Manganese, with a current of 380 ampères and 80 volts, volatilises very readily; 400 grams of the metal left only a small residue of the carbide after heating for ten minutes. Iron, with 350 ampères and 70 volts, volatilises, and condenses as a grey powder mixed with some very brilliant, malleable scales. Uranium, with 350 ampéres and 75 volts, volatilises readily, and condenses in small, non-magnetic spheres free from carbon.

Silicon volatilises with 380 ampères and 80 volts, and condenses in small spheres, mixed with a grey powder and a small quantity of silica. Carbon, with 370 ampères and 80 volts, rapidly changes into graphite and then volatilises, condensing in very light, thin, translucid, maroon-coloured plates, similar to or identical with the maroon-coloured variety of carbon observed by Berthelot. It burns easily in oxygen.

Calcium oxide, with 350 ampères and 70 volts, volatilises after 8 or 10 minutes, and with 400 ampères and 80 volts it volatilises in five minutes. The oxide condenses entirely as an amorphous powder. With 1000 ampères and 80 volts, 100 grams of the volatilised oxide can be obtained in five minutes.

Magnesium oxide is more difficult to volatilise than calcium oxide, and its boiling point is near its melting point. With 360 ampères and 80 volts, it gives off a quantity of vapour; and with 1000 ampères and 10 volts, distillation becomes very rapid. C. H. B.

Discoverer of the Method of determining the Density of Solids by Suspension. By W. Ostwald (*Zeit. physikal. Chem.*, **12**, 94).—The author points out that the discoverer of the method of finding the density of solids by suspension is not Dufour, as Retgers

states, but Davy, who determined (in 1808) the specific gravity of sodium by finding the proportions in which sassafras oil (sp. gr. 1·096) and naphtha (sp. gr. 0·861) must be mixed in order to produce a liquid in which the metal remains suspended without sinking or floating. J. W.

Formation of Supersaturated Solutions. By A. L. POTILITZIN (*J. Russ. Chem. Soc.*, **25**, 73—75).—The following rule regarding the formation of supersaturated aqueous solutions is stated by the author. Only those saline hydrates can form supersaturated solutions whose dissociation tension in dry air at the ordinary temperature is considerable. Salts containing water of crystallisation, which do not decompose at the ordinary temperature in dry air or in a vacuum, or decompose only very slowly, are incapable at that temperature of giving supersaturated solutions.

The behaviour of the chlorates and bromates of the alkaline earths is cited in illustration. J. W.

Influence of Hydration on Solubility. By N. S. KURNAKOFF (*J. Russ. Chem. Soc.*, **24**, 629—631).—Le Chatelier stated the rule that when a substance forms two hydrates, the hydrate containing least water is more soluble than the higher hydrate at any temperature below the point of transformation. The author finds a great number of apparent exceptions to this rule amongst the ammonio-metallic compounds. For example, the chlorides and nitrates of the roseopentamine bases $MX_3,5NH_3,H_2O$ (where M = Co, Cr, or Ir) are much more soluble than the corresponding anhydrous forms $MX_3,5NH_3$, the purpureopentamine salts. He also mentions the fact that organic anhydrides (acid anhydrides, lactones, oxides, &c.) are less soluble in water than the corresponding hydrated compounds.

The following solubilities were found by V. Meyer's method for various ammonia compounds of cobalt.

	100 parts of water dissolve		
Temp.	$CoCl_3,5NH_3$.	$CoCl_3,5NH_3,H_2O$.	$CoCl_3,6NH_3$.
0°	0·232	16·12	4·26
16·9°	—	24·87	—
46·6°	1·031	—	12·74

J. W.

Non-electrolytic Dissociation in Solutions. By M. WILDERMANN (*Ber.*, **26**, 1773—1786).—In salt solutions the author recognises two sorts of dissociation, electrolytic dissociation into ions and a non-electrolytic dissociation of larger molecular aggregates of the dissolved substance into smaller. Thus, in a solution of potassium chloride, the following substances may be assumed to exist, K_2Cl_2, KCl, $\overset{+}{K_2}\overset{-}{Cl}$, $K\overset{-}{Cl_2}$, $\overset{+}{K}$, and $\overset{-}{Cl}$. The author is of opinion that this additional assumption of non-electrolytic dissociation is sufficient to explain the divergencies existing between the observed data and the values calculated on the electrolytic dissociation hypothesis alone.

In the present paper, he discusses the electrical conductivity of salt solutions which do not in general obey the dilution law applicable to weak acids and bases. From an imperfect mathematical discussion, based on the above assumption, he deduces formulæ which show a qualitative agreement with the experimental data. J. W.

The Colour of the Ions. By G. Magnanini (*Zeit. physikal. Chem.*, **12**, 56—72).—Ostwald, from his researches on the absorption spectra of solutions of the permanganates, rosolates, chromoxalates, &c., drew the conclusion that the absorption depended on the colour of the ions in the solution and not on that of the undissociated molecules of the dissolved salt, for all permanganates, for example, gave precisely the same absorption in dilute solutions. The author contests this conclusion, and shows that the salts of violuric acid give red solutions, whilst violuric acid itself gives colourless aqueous solutions, although it is dissociated to the extent of 8 per cent. at a dilution of 256. It cannot, therefore, be the negative ion which causes the absorption in the salt solution, nor can it be the positive metallic ion; so that the colour must come from the undissociated part. The absorption for equivalent solutions of potassium, sodium, and ammonium violurates is equal. Addition of large excess of potassium nitrate to a solution of potassium violurate does not influence the absorption, although it diminishes the degree of dissociation.

J. W.

Influence of Dilution on the Velocity of Chemical Reactions. By V. Omelyansky (*J. Russ. Chem. Soc.*, **24**, 647—663).—The author has investigated the influence of dilution on the velocity constant of two reactions, namely:—

I. $\text{Iso-}C_4H_9(OH) + (C_2H_3O)_2O = CH_3{\cdot}CO{\cdot}C_4H_9O + C_2H_4O_2$

in benzene solution, and

II. $NEt_3 + EtI = NEt_4I$

in acetone solution.

In the first column of the following table is given the dilution V, in the second the velocity constant K, and in the third their product. The measurements were made at 100°.

I.

V.	K.	KV.
1·0 (without solvent)	0·212	0·212
2·0	0·178	0·356
4·0	0·123	0·492
6·0	0·102	0·612
16·0	0·0401	0·641
40·9	0·0165	0·674
61·6	0·0107	0·659
79·8	0·00875	0·698
101·0	0·00682	0·692
149·6	0·00457	0·682
303·7	0·00220	0·668

II.

V.	K.	KV.
16·0	0·0676	1·08
40·9	0·0280	1·14
61·0	0·0209	1·27
80·3	0·0159	1·27
100·8	0·0122	1·11
151·2	0·00805	1·21

From these tables it appears that after the reacting substances have been diluted with 15 times their volume of solvent, the constant of velocity of a bimolecular reaction is inversely proportional to the dilution. J. W.

Vapour Tensions of Solutions of Sulphur and Phosphorus in Carbon Bisulphide. By G. Guglielmo (*Real. Accad. Linc.*, 1892, ii, 210—216.—The author has measured the vapour tensions of solutions of sulphur and phosphorus in carbon bisulphide by enclosing them in a space exhausted by a Sprengel pump, and measuring the vapour pressure by means of a manometer. For solutions at ordinary temperatures, a glass apparatus was used consisting of two bulbs, one to contain pure carbon bisulphide, the other to hold the solution; these vessels could be isolated from each other and from the pump by means of suitably-arranged mercury traps. In such an apparatus, the vapour tension of the pure carbon bisulphide is first determined, then that of the solution; the ratios of the differences of the two pressures to the vapour tension of carbon bisulphide at the corresponding temperatures are therefore proportional to the number of dissolved molecules per unit of solution. In the case of sulphur, the experiments were conducted between 0° and 13·8°, and show that for solutions up to 20 per cent., the molecular depression of the vapour tension corresponds with a sulphur molecule containing 8 atoms for the more dilute solutions, increasing to 9 for the more concentrated.

The vapour tensions of several carbon bisulphide solutions of phosphorus were measured at 0°; the depressions of the vapour tensions correspond approximately with a tetratomic molecule for dilute solutions (3 per cent.), just as is found by vapour density determinations. As would be expected, the molecular weight increases for more concentrated solutions.

The solutions are kept stirred by means of steel rods, which are enclosed in the exhausted bulbs, and are moved up and down by the motion of a horseshoe magnet outside. W. J. P.

Determination of Molecular Weights by Beckmann's Method. By G. Baroni (*Gazzetta*, **23**, i, 263—277).—In this preliminary communication, the author gives a number of data for the boiling points of aqueous solutions of boric acid, potassium chloride and bromide, sodium chloride, and barium chloride. The immediate continuation of the investigation is interrupted by an accident. W. J. P.

Phenanthrene as a Solvent in Cryoscopic Determinations. By F. Garelli and A. Ferratini (*Gazzetta*, **23**, i, 442—452).—The authors have previously suggested (Abstr., 1892, 156) that the abnormal values deduced from cryoscopic determinations of the molecular weight of indole in naphthalene solution, result from the formation of solid solutions of indole in the crystallising hydrocarbon; they suspected also that the formation of such solid solutions was in some way influenced by similarity of constitution between the solvent and the dissolved substance. It is now found that the crystals which separate on cooling a liquid solution of carbazole in phenanthrene, two substances of very analogous constitution, contain a large quantity of the dissolved substance; the crystals deposited from a liquid solution containing 7·5 per cent. of carbazole contained 11·42 per cent. of the latter, whilst a 7·5 per cent. solution of diphenylamine in phenanthrene deposited crystals containing only 5·39 per cent. of the amido-compound.

The abnormally small depressions of the freezing points of hydrocarbons and allied compounds by benzoic acid have been remarked by several investigators. Benzoic acid also gives too small a depression of the freezing point of phenanthrene, and the authors suppose that this may be found a general rule for organic acids.

Apart from the great difficulty experienced in purifying phenanthrene, the authors consider it a better solvent for use in cryoscopic determinations than naphthalene; its high constant of depression (120) renders it possible to work accurately with very dilute solutions, whilst its small tendency to volatilise makes it more easy of manipulation than naphthalene. A satisfactory series of test experiments with naphthalene, diphenylamine, thymol, stilbene, metadinitrobenzene, and *n*-methylcarbazole is given in illustration of this.

W. J. P.

Cryohydric Temperatures. By F. A. H. Schreinemakers (*Zeit. physikal. Chem.*, **12**, 73—93).—Guthrie made some experiments on the cryohydric points of systems of mixed salts, but did not arrive at any general conclusion. The author now discusses the question from the theoretical standpoint, and makes the following deductions.

When the two salts do not form a double salt, the cryohydric point of the mixture is lower than the cryohydric point of a solution in equilibrium with either of the salts separately. This conclusion receives confirmation both from Guthrie's and from the author's experiments.

When a double salt is formed which decomposes on dissolution, such as $PbI_2,KI,2H_2O$, the cryohydric temperature of a solution in equilibrium with the double salt and one of its components is lower than the cryohydric temperature of a solution in equilibrium with this component alone; and the cryohydric point of a solution in equilibrium with the double salt and the component which is not deposited is lower than that of a solution in equilibrium with the double salt and the component which is deposited.

When a double salt is formed which dissolves homogeneously without decomposition, such as $CuSO_4.(NH_4)_2SO_4,6H_2O$, the cryohydric temperature of a solution in equilibrium with the double salt

and one of its components is lower than the cryohydric temperature of a solution of the double salt alone.

These conclusions have been confirmed by experiment. J. W.

Osmotic Pressure. By A. Naccari (*Gazzetta*, **23**, i, 535—537).—A porous cell, containing a semi-permeable membrane of copper ferrocyanide and fitted with a manometer, is partially filled with sugar solution and placed in pure water; water then passes into the cell, and the osmotic pressure set up is measured by the manometer. The cell is now placed in a more concentrated sugar solution than that which it contains, and water passes out; by reducing the atmospheric pressure in the cell, equilibrium is established between the internal and external sugar solutions, although the pressure inside is not so great as the osmotic pressure set up when the cell stood in pure water and contained the same volume of solution. The author concludes from this experiment that if Boyle's law were applicable to liquid solutions, it should be possible for a gas at constant volume and temperature to exert any given pressure, and that hence the theory of osmotic pressures is faulty. W. J. P.

Note by Abstractor.—The osmotic pressure in such experiments as the above is, of course, measured by counterbalancing it against an equal and known gaseous pressure; consequently, in the second part of the author's experiment the pressure registered on the manometer is simply the difference of the osmotic pressures of the two sugar solutions which are in equilibrium, and nothing is proved against the theory of osmotic pressures. W. J. P.

Relation between the Periodic Classifications of L. Meyer and Mendeléeff. By U. Alvisi (*Gazzetta*, **23**, i, 509—517).—The author endeavours to trace a relation between the equivalents and specific gravities of the elements by means of the differences of the numerical values of these two functions. W. J. P.

Specific Gravities of the Elements in the Periodic System. By U. Alvisi (*Gazzetta*, **23**, i, 518—523).—In L. Meyer's or Mendeléeff's classification of the elements, the sum of the specific gravities of the elements on one half of any period is approximately equal to the sum of those on the other half. W. J. P.

Stereochemistry or Motochemistry? By E. Molinari (*J. pr. Chem.* [2], **48**, 113—135).—By the term "motochemistry," the author implies the hypothesis that the constitution of compounds is dependent on the intramolecular movements of the atoms in relation to each other, rather than on the relative positions of the atoms in space. The hypothesis treats the bonds by which it is customary to represent the union of atoms as signifying the nature of the swing or energy of the atoms with regard to each other. Thus, doubly linked and singly linked carbon atoms are of different value in respect of the energy of their movement with regard to each other, and double or treble bonds signify excess of energy, ready to be exerted in saturating the com-

pound. The author applies his hypothesis to the benzene ring, and shows that only one ortho-bi-substitution product is possible. Motoisomerism involves asymmetry, but the term must be used in a greatly extended sense, the phenomenon depending on the mass and valency of the atoms or atomic groups, as well as on their number and nature. Motoisomerides will exist in those cases in which it is possible for the order of approachment of the (in this sense) asymmetrical carbon atom towards its neighbouring atoms to vary. Thus, in the case of benzilmonoxime, $COPh{\cdot}C\lessdot^{N{\cdot}OH}_{C_6H_5}$, it is possible for two motoisomerides to exist; for if the swing between carbon and carbon be designated by *a*, and that between carbon and nitrogen by *b*, the isomerides will be represented by (1) *a*, *a*, *b*, *b*, and (2) *a*, *b*, *a*, *b*.

The author adduces a number of other examples of the application of this hypothesis. A. G. B.

Inorganic Chemistry.

Iodine Monochloride. By S. Tanatar (*J. Russ. Chem. Soc.*, **25**, 97—101).—To prepare the β-modification of iodine monochloride of melting point 13·9°, the author places the liquid chloride in a vessel with a drawn-out neck, and heats very slowly so that the walls become covered with crystals of the trichloride. The heating is continued until the boiling point of the liquid is reached and all the trichloride expelled through the constricted neck, which is then sealed off. On cooling, first to the atmospheric temperature and afterwards to −10°, no trichloride should be deposited on the upper parts of the vessel. If any such separation takes place, the boiling must be renewed, for no β-monochloride can be formed in presence of trichloride. When the β-modification is once formed, it is very stable as long as it is kept in the sealed vessel. When melted and cooled in a sealed tube to −20°, it passes into the α-modification, from which it may be reobtained by again melting and cooling to −10°.

The heat of transformation of the β-chloride into the α-modification is 0·273 Cal., and the heat of fusion of the α-chloride is −2·32 Cal. The sp. gr. of liquid iodine monochloride is 3·2856 at 16°/16° and 3·2402 at 34°/34°. J. W.

Densities of the Principal Gases. By Lord Rayleigh (*Proc Roy. Soc.*, **53**, 134—149).—The author describes in some detail the manometric gauge, and the connections of the globe with pump and manometer, which he has employed in his new experiments on the densities of air, oxygen, and nitrogen.

The oxygen was prepared in three ways—(*a*) from chlorates, (*b*) from potassium permanganate, and (*c*) by electrolysis. The air

drawn from outside was passed through potash solution, then through tubes filled with fragments of solid potash, and finally over phosphoric anhydride. The nitrogen was prepared by passing air through a potash solution, over reduced copper, then through a U-tube to deposit water, again over heated copper, and finally over heated copper oxide. The following table is given of the densities of oxygen, nitrogen, and hydrogen referred to that of air as unity.

	Oxygen.	Nitrogen.	Hydrogen.
Regnault (corr.).....	1·10562	0·97138	0·06949
v. Jolly (corr.)	1·10502	0·97245	—
Leduc	1·1050	0·9720	0·06947
Rayleigh	1·10535	0·97209	0·06960
Mean.....	1·10525	0·97218	0·06952

The density of hydrogen was calculated from that of oxygen, using the ratio 15·882. The mean of the best densities under standard conditions referred to water at 4° as 1000, that is, the weight of 1 litre in grams, is :—

Air.	Oxygen.	Nitrogen.	Hydrogen.
1·29347	1·42961	1·25749	0·08991

J. W.

Electrolysis of Steam. By J. J. Thomson (*Proc. Roy. Soc.*, **53**, 90—110).—A current of steam was passed through the middle limb of a T-tube, the closed side limbs of which were furnished with delivery tubes, and also with gold or platinum electrodes between which sparks might be passed through the steam. The delivery tubes conducted the gases into two eudiometers, in which the gaseous mixture formed on passage of the sparks was exploded. When the sparks were from 1·5 to 4 mm. long it was observed that, within the limit of error of the experiment, the volumes of the excess of hydrogen in the one tube and of oxygen in the other, which remain after the explosion of the mixed gases, are respectively equal to the volumes of the hydrogen and oxygen liberated in a water voltameter placed in series with the steam tube; and that the excess of hydrogen appears in the tube which is in connection with the positive electrode, the excess of oxygen in the tube which is in connection with the negative electrode. When the spark length is greater than 4 mm., the first of the preceding results ceases to hold, and when the spark length is increased to over 11 mm., the excess of hydrogen, instead of appearing at the positive electrode, changes over to the negative, the excess of oxygen at the same time going over from the negative to the positive electrode. When the sparks are very much longer, about 22 mm., reversal again takes place, the hydrogen appearing at the positive electrode.

The author finds that when the arc discharge passes through hydrogen and oxygen respectively, the hydrogen behaves as if it had a negative charge, and the oxygen as if it had a positive one.

J. W.

Composition of Water by Volume. By A. Scott (*Proc. Roy. Soc.*, **53**, 130—134).—The author has continued his investigation of

the proportions by volume in which oxygen and hydrogen unite, using improved apparatus. The taps were lubricated with syrupy phosphoric acid instead of vaselin, which was found to introduce traces of the oxides of carbon into the gases; and the measurements were all made at constant volume by varying the pressure. The oxygen was prepared from silver oxide, and the hydrogen from sodium and steam. In some experiments the hydrogen was further treated by absorption in palladium.

The mean ratio of hydrogen to oxygen was found in 5 series of 53 experiments to be:—

2·002435 ± 0·00006, impurity in both gases equally,
or 2·002431 ± 0·00006, „ hydrogen alone.

If six experiments were rejected, the value would be 1·002466 ± 0·000003, any impurity making no difference, whether assumed to be all in the hydrogen or equally distributed between the two gases. The most probable value is 2·00245, which, combined with Rayleigh's value, 15·882, for the ratio of the densities of the gases, gives 15·862 for the atomic weight of oxygen, hydrogen being 1, and 1·0078 for the atomic weight of hydrogen, oxygen being taken as 16. J. W.

Density, &c., of Sulphurous Anhydride. By A. Leduc (*Compt. rend.*, **117**, 219—222).—Under normal conditions of pressure and temperature, the density of gaseous sulphurous anhydride is 2·2639, with an estimated error of 1/10,000th of the value. The gas investigated was prepared from pure sulphuric acid and pure mercury, in an apparatus without rubber connections, and was dried with sulphuric acid and phosphoric anhydride.

The author finds the following formula to express the relation between the weight of the gas at a pressure p (from 1 to 0·5 atmosphere) and that at the normal pressure.

$$W_{760} = W_p \frac{760}{p} [1 + 323 \times 10^{-7}(760 - p)].$$

The mean coefficient of expansion of the gas between 0° and 20° at normal pressure was found to be 0·00396, the true coefficient at 0° being 0·003978. Under a pressure of 334 mm. the mean coefficient of expansion is 0·003787 between 0° and 22°. The coefficient of increase of pressure with the temperature is 0·003883 at 0°.

J. W.

Preparation of Ammonium Persulphate. By K. Elbs (*J. pr. Chem.* [2], **48**, 185—189; compare Marshall, Trans., 1891, 771).—A porous clay cell (80—100 c.c. capacity), containing a saturated solution of ammonium sulphate in a mixture of 1 part by volume of sulphuric acid with 8 parts by volume of water, is placed in a beaker and surrounded by a mixture of equal volumes of sulphuric acid and water. A lead cylinder, placed round the porous cell, serves as the cathode, and a platinum spiral having a surface of 0·5 sq. cm. is suspended inside the porous cell to serve as the anode. The beaker is imbedded in ice. The electrolysis is effected by a current of 2—3

ampères ; some 8 volts will be necessary when the internal resistance of the decomposing cell is about 1 ohm. After 2—3 hours, the contents of the porous cell are filtered through glass wool and the crystals of ammonium persulphate dried on a porous plate ; the filtrate is shaken with ammonium sulphate and once more electrolysed. 20—40 grams of the persulphate may thus be obtained in one operation, the yield being least at the outset, when the liquid is being saturated with the persulphate. The sulphuric acid in the outer cell eventually becomes alkaline from the transit of the ammonium ion, and *pari passu* the ammonium sulphate in the inner cell becomes strongly acid ; from time to time the former liquid must be renewed and the latter nearly neutralised with ammonia. To recover the persulphate left in the liquor when the preparation has been completed, a concentrated solution of potassium carbonate or acetate is added ; potassium persulphate will thus be precipitated, as 100 parts of water only dissolve 2 parts of this salt, whereas they dissolve 65 parts of the ammonium salt.

Ammonium persulphate, thus prepared, contains some 3—5 per cent. of impurities, consisting chiefly of ammonium sulphate, but partly of ammonium alum, derived from the clay of the porous cell. It may be recrystallised from water. A. G. B.

Atomic Refraction of Boron. By A. Ghira (*Gazzetta*, **23**, i, 452—462).—The author has determined the refraction constants of a number of compounds of boron for the line D and the α, β, and γ hydrogen lines ; the results obtained for the D and H_α lines are summarised in the following tables.

Substance.	Temp.	$P\frac{\mu_D - 1}{d}$.	$P\frac{\mu_D^2 - 1}{d(\mu_D^2 + 2)}$.	Atomic refraction of boron.	
				From μ.	From μ^2.
$B(OEt)_3$	6·2°	63·30	38·57	5·04	3·24
$B(OC_4H_9\beta)_3$	7·8	109·68	66·31	5·52	3·37
$B(OC_5H_{11}\beta)_3$	9·7	132·60	79·88	5·49	3·12
$B(OC_3H_5)_3$	8·3	84·18	50·69	3·87	2·73

Substance.	Temp.	$P\frac{\mu_{H_\alpha} - 1}{d}$.	$P\frac{\mu_{H_\alpha}^2 - 1}{d(\mu_{H_\alpha}^2 + 2)}$.	Atomic refraction of boron.	
				From μ.	From μ^2.
BCl_3	5·7°	34·62	20·86	5·32	2·80
BBr_3	—	51·03	29·69	5·13	2·84
$B(OEt)_3$	6·2	63·00	38·41	5·10	3·19
$B(OC_4H_9\beta)_3$	7·8	109·13	66·01	5·63	3·43
$B(OC_5H_{11}\beta)_3$	9·7	131·90	79·50	5·60	3·24
$B(OC_3H_5)_3$	8·3	83·83	50·32	3·73	2·32

The author also gives the refraction for the rays H_β and H_γ, and thence calculates the dispersion for H_α—H_γ. The specific gravities employed are referred to water at 4°; the atomic refractions of other elements than boron, used in the calculations for the hydrogen lines, are those of Nasini and Costa (Abstr., 1891, 1305), for the D line those of Conrady and Zecchini (this vol., ii, 253).

The author has also made observations on aqueous solutions of boric anhydride; little weight, however, attaches to these results, owing to the fact that less than 2 per cent. solutions had to be employed. W. J. P.

Combination of Boron Bromide with Phosphorus Tribromide. By TARIBLE (*Compt. rend.*, **116**, 1521—1524).—Boron bromide was prepared in large quantity by the action of bromine on amorphous boron, obtained by Moissan's method of reducing boric anhydride by means of magnesium. In presence of carbon bisulphide, it combines readily with phosphorus tribromide in molecular proportion, forming the compound PBr_3,BBr_3, which separates in beautiful, colourless needles after half the solvent has been distilled off and the residual liquid is cooled. These crystals melt at about 61°, dissolve in carbon bisulphide and in chloroform, fume in moist air, and are very easily decomposed by water with formation of boric, phosphorous, and hydrobromic acids. When heated in a current of hydrogen, it sublimes with partial decomposition; in a current of oxygen, it decomposes slightly at the ordinary temperature, and takes fire below a red heat. Sulphur, bromine, iodine, and other non-metals are without action on it, but chlorine at the ordinary temperature converts it into the compound PCl_5,BCl_3.

Boron phosphorus bromide crystallises unchanged from both phosphorus tribromide and boron bromide, and hence would seem to be the only stable compound of these two substances.

The compound PBr_5,BBr_3 is obtained in small, white crystals by pouring a carbon bisulphide solution of phosphorus pentabromide into a similar solution of boron bromide. It is only slightly soluble in cold carbon bisulphide, but dissolves readily on heating, and can be recrystallised from this solvent. When heated in sealed tubes, it melts at 140°; but when heated with exposure to air, it volatilises at about 105° without melting. When exposed to the air, it fumes, and it is energetically decomposed by water, with formation of boric, phosphoric, and hydrobromic acids. Pure and dry hydrogen is without action on it even when heated, but it burns when heated to redness in oxygen, and is completely decomposed by chlorine with great development of heat. It absorbs ammonia at the ordinary temperature with development of heat, and yields a white, crystalline compound. No evidence could be obtained of the existence of any other compound of phosphorus pentabromide and boron tribromide.

C. H. B.

Bromoborates. By G. ROUSSEAU and H. ALLAIRE (*Compt. rend.*, **116**, 1445—1446; compare this vol., ii, 468).—*Iron bromoborate*, $6FeO,8B_2O_3,FeBr_2$, is readily obtained by passing bromine vapour

over an intimate mixture of boronatrocalcite with a large excess of fragments of iron wire heated to redness. It forms a mixture of greyish-white cubes and octahedra which act on polarised light in the same way as natural crystals of boracite, and are larger the higher the temperature. They are mixed with black prisms of ferric borate, which can be removed by treatment with cold, concentrated hydrobromic acid. Iron bromoborate dissolves slowly in warm nitric acid.

Zinc bromoborate, $6ZnO,8B_2O_3,ZnBr_2$, forms white, microscopic, pseudo-cubic crystals, which also act on polarised light. It is obtained by the action of zinc bromide vapour on calcium borate, heated to redness in an atmosphere of carbonic anhydride.

C. H. B.

Cyclic Condensation of Carbon. Artificial Production of the Diamond. By G. Rousseau (*Compt. rend.*, **117**, 164—167).—When barium and strontium manganites are heated, they undergo a cyclic change, a salt such as MnO_2,BaO being formed at 800°, changing to $2MnO_2,BaO$ at 1000—1200°, and reverting again to MnO_2,BaO at a white heat. A similar change occurs when sodium manganite is heated. By treating hydrocarbons in this manner, it seemed probable, since each of the modifications of carbon is known to have a temperature or zone of temperature of maximum stability, that an analogous change might be produced, and this proved to be the case. Acetylene was generated from calcium carbide and steam in a lime crucible, heated in an electric furnace; after 1½ hours, several particles of black diamond were found to have been formed; whilst in the cooler parts of the crucible, graphite was deposited in black, microscopic leaflets, identical with those of natural plumbago. In a second experiment, the carbide was decomposed by moist coal gas, the decomposition of which furnished an additional supply of acetylene; 20 milligrams of diamond was obtained.

The diamonds, some of which were as much as 0·5 mm. in diameter, formed wrinkled, brownish-black, roundish masses, sometimes covered with white, brilliant points, more or less crystalline in character. They remained unattacked by potassium chlorate and nitric acid mixture, by potassium hydrogen sulphate, and by hydrofluoric acid. They scratched corundum, and, when burned, left a cellular ash. It is noteworthy that the formation took place under atmospheric pressure.

Jn. W.

Solubility of "Insoluble" Salts. By A. F. Holleman (*Zeit. physikal. Chem.*, **12**, 125—139).—The author has investigated the electrical conductivity of aqueous solutions of the so-called insoluble salts, and from his numbers calculates the actual solubility.

In the case of precipitated calcium sulphate, the dilution (in equivalents) of the saturated solution was found to be $v = 36·9$ at 15°, whilst by evaporation and weighing, $v = 37·4$ was obtained. Other check determinations gave equally concordant results.

The following are the values obtained:—

1 part of	$BaSO_4$	dissolves in	429,700	parts of water at	18·4°
,,	,,	,,	320,000	,, ,,	37·7
,,	$SrSO_4$	,,	10,070	,, ,,	16·1
,,	,,	,,	10,030	,, ,,	26·1
,,	AgCl	,,	715,800	,, ,,	13·8
,,	,,	,,	384,100	,, ,,	26·5
,,	AgBr	,,	1,971,650	,, ,,	20·2
,,	,,	,,	775,400	,, ,,	38·4
,,	AgI	,,	1,074,040	,, ,,	28·4
,,	,,	,,	420,260	,, ,,	40·4
,,	$CaC_2O_4,2Aq$	,,	148,220	,, ,,	13·6
,,	,,	,,	124,400	,, ,,	24·0
,,	$BaCO_3$	,,	64,070	,, ,,	8·8
,,	,,	,,	45,566	,, ,,	24·2
,,	$SrCO_3$	,,	121,760	,, ,,	8·8
,,	,,	,,	91,468	,, ,,	24·3
,,	$CaCO_3$	,,	99,500	,, ,,	8·7
,,	,,	,,	80,040	,, ,,	23·8

From the solubilities at the different temperatures, the heats of precipitation were calculated, the results showing fair accordance with the observed thermochemical values. J. W.

Method for reducing Metallic Oxides. By W. H. Greene and W. H. Wahl (*Chem. News*, **68**, 3—4).—For the production of alloys, the use of metallic silicides is suggested as more beneficial than reduction by carbon. For example: 128 lbs. of a metallic alloy having the composition Fe, 70; Mn, 29; C, 0·7; Si, trace, may be obtained by melting on the furnace hearth or in a crucible a charge of 100 lbs. of ferrosilicon (containing Si, 10 per cent., and C, 1 per cent.), and adding 70 lbs. of manganous oxide and 50 lbs. of lime. The reaction takes place quickly, the silicon seizing the oxygen of the manganous oxide and fluxing with the lime, manganous oxide, and alumina present; therefore, the manganous oxide has to be added in larger quantity than is required by theory. By substituting other oxides for the manganous oxide, ferro-alloys have been obtained containing 50 per cent. of nickel, or 20 per cent. of chromium, or 50 per cent. of tungsten; in all these, the carbon may be reduced so low as to meet all requirements of commerce. The method is applicable to other metals besides iron. D. A. L.

Action of Carbonic Oxide on Sodammonium and on Potassammonium. By A. Joannis (*Compt. rend.*, **116**, 1518—1521).—When pure and dry carbonic oxide is passed into a solution of potassammonium in liquefied ammonia at about −50°, the blue colour gradually becomes weaker, and at last changes to pink. At this point the reaction is complete, and if the ammonia is allowed to evaporate, the compound *potassium carbonyl*, $K_2C_2O_2$, is obtained as a pale, rose-coloured powder which detonates in contact with air or water, or when heated to 100°. If, however, it is allowed to come in

contact with water *vapour* in a vacuum, it deliquesces and forms a yellow solution.

Sodium carbonyl, $Na_2C_2O_2$, is a white powder with a lilac tint, and is obtained in a similar manner. It detonates at 90°, or when brought in contact with air or water, but deliquesces quietly in contact with water vapour in a vacuum. When it detonates, very little gas is evolved, and a small quantity of sodium cyanide is formed, but the principal reaction is represented by the equation $2Na_2C_2O_2 = Na_2CO_3 + Na_2O + C_3$. When detonation takes place in presence of water, the small quantity of gas evolved contains 86 per cent. of hydrogen and 14 per cent. of carbonic oxide. C. H. B.

Quantitative Separation of Cæsium and the Preparation of Pure Cæsium and Rubidium Compounds. By H. L. Wells (*Zeit. anorg. Chem.*, **4**, 341—345; and *Amer. J. Sci.*, **46**, 186).—The solubility of the double salt Cs_2PbCl_6 in a solution of equal parts of fuming hydrochloric acid and water, saturated with chlorine and containing twice the theoretical quantity of lead chloride, is 0·000068 gram Cs_2PbCl_6 for 1 c.c. In concentrated hydrochloric acid, in the presence of excess of lead chloride, the solubility is 0·000049 gram per c.c. Under the same conditions, the solubility of the salt Rb_2PbCl_6 is 0·003 gram per c.c. From a solution containing cæsium and potassium, the cæsium is precipitated as Cs_2PbCl_6 by chlorine in the presence of lead chloride and hydrochloric acid, and the precipitate dried at 100°, and weighed; or decomposed by hot water, and the cæsium determined in the filtrate as sulphate. The results are about 4 per cent. too low.

From a solution containing cæsium, rubidium, potassium, sodium, and lithium, the cæsium and rubidium are precipitated as the double salts, with lead tetrachloride, dried at 100°, and weighed; then converted into the sulphates, and again weighed. The determinations of the cæsium are fairly good. Part of the rubidium, however, remains in the solution, and can be precipitated, together with the potassium, by means of platinic chloride.

The preparation of pure cæsium and rubidium salts from their minerals is carried out as follows: They are first separated in the form of the double salts with lead tetrachloride; the latter are decomposed with water, the solution treated with a slight excess of ammonium sulphide to free it from lead, and the filtrate evaporated to dryness; the mixed chlorides of cæsium and rubidium are dissolved in concentrated nitric acid, the solution evaporated to dryness, the residue dissolved in water, excess of oxalic acid added, and the mixture again evaporated to dryness and heated in a platinum crucible until the oxalates are completely converted into carbonates. The rubidium is then separated as acid oxalate, and the cæsium as cæsium antimony chloride. E. C. R.

Action of Zinc and Magnesium on Solutions of Metallic Salts. Estimation of Potassium. By A. Villiers and F. Borg (*Compt. rend.*, **116**, 1524—1527).—Estimations of metals such as copper and platinum, by precipitating them from solutions of their

salts by means of metallic zinc, are usually inaccurate, even when the zinc is pure, in consequence of the formation of alloys of variable composition.

Magnesium behaves differently, and can be used for the accurate estimation of copper, gold, and platinum, provided the solution contains no other metals except those of the alkalis and alkaline earths. The copper, &c., is precipitated in a granular form which is easily washed. In presence of metals other than those specified, alloys are formed even in a strongly acid solution.

This reaction can be applied to the estimation of potassium. The platinochloride is precipitated, washed with a mixture of equal volumes of absolute alcohol and ether, then dissolved in hot water, acidified with hydrochloric acid, and gradually mixed with excess of magnesium. The precipitated platinum is washed, heated, and weighed. The method is very accurate, and can be applied to the impure platinochloride obtained by the precipitation of various commercial potassium compounds, when the weight of the salt would give inaccurate results, whilst the weight of reduced platinum gives accurate results. This is true also of precipitates formed in the presence of bromides. C. H. B.

Ternary Alloys. Part VII. By C. R. A. Wright (*Proc. Roy. Soc.*, **52**, 530—543; compare this vol., ii, 415).—The author has prepared a number of alloys consisting of lead or bismuth, aluminium or zinc, and cadmium or antimony, molten lead, bismuth, and zinc being miscible with cadmium or antimony in all proportions. The close analogy previously noted between aluminium and zinc is not shown in these alloys, partly because cadmium and aluminium (contrary to statements in text-books) are not completely miscible, and partly because aluminium and antimony form a compound, AlSb, which melts at 1045°; the discussion of these alloys is therefore postponed for the present. In the case of the mixtures of lead, zinc, and cadmium, the ratio of lead and zinc corresponds with the formula Pb_4Zn, and that of lead and cadmium to Pb_2Cd. The composition at the limiting point was: lead, 36·5; zinc, 2·9; cadmium, 60·6. At the limiting point of the mixture of bismuth, zinc, and cadmium, the composition was: bismuth, 19·5; zinc, 28·5; cadmium, 52·0, corresponding with a ratio represented by the formula $BiZn_3$. A comparison of the critical curves of this and the preceding alloy shows that the substitution of bismuth for lead depresses the curve. In the case of the mixtures of lead, zinc, and antimony, the values at the limiting point were: lead, 38·1; zinc, 35·4; antimony, 26·5; the ratio of lead to zinc corresponding with the formula $PbZn_3$. The composition of the analogous bismuth alloy at the limiting point was: antimony, 17·50; bismuth, 22·75; zinc, 59·75, corresponding with the formula $BiZn_8$; in this case, the limiting point coincided with the highest point of the curve; further, the curve with cadmium as solvent lies outside the one deduced with tin as solvent, that with antimony as solvent inside; the temperature of experiment in all three series being 600—650°. J. B. T.

Double Chlorides of Lead and Ammonium. By W. W. RANDALL (*Amer. Chem. J.*, **15**, 494—504).—André (Abstr., 1883, 717, 903) has described a number of double chlorides of ammonium and lead whose formulæ are not in accord with the law which Remsen has enunciated as controlling the composition of double haloïd salts (Abstr., 1889, 934). The author has endeavoured to prepare the double salts described by André, but in most cases crystallographic examination showed that the substances prepared were mixtures, not individual compounds. The only salts which appeared homogeneous under the microscope were $2PbCl_2,NH_4Cl$ and $PbCl_2,2NH_4Cl$, both of which are in accord with Remsen's law. A. G. B.

Double Salts of Lead Tetrachloride. By H. L. WELLS (*Zeit. anorg. Chem.*, **4**, 335—340, and *Amer. J. Sci.*, **46**, 180).—The salts are yellow and crystallise in regular octahedra. They are decomposed by water with the formation of lead peroxide and chlorine. The cæsium salt is less readily decomposed than the others. They are also decomposed by boiling with excess of hydrochloric acid; and in this case also the cæsium salt is decomposed less readily. The cæsium salt is almost insoluble in concentrated solutions of cæsium chloride and in hydrochloric acid in the presence of free chlorine. The salts can be washed with hydrochloric acid containing chlorine, and are not decomposed by exposure to air. The corresponding sodium and calcium salts could not be prepared.

Ammonium plumbichloride, $(NH_4)_2PbCl_6$, is prepared by adding a cold, saturated solution of ammonium chloride in dilute hydrochloric acid to a solution prepared by dissolving lead peroxide in hydrochloric acid at 0°.

Potassium plumbichloride, K_2PbCl_6, is obtained by mixing equal volumes of a saturated solution of potassium chloride and lead chloride in hydrochloric acid saturated with chlorine, and of a similar solution, which does not contain potassium chloride.

Rubidium plumbichloride, Rb_2PbCl_6, is obtained by treating a solution of rubidium chloride and lead chloride in dilute hydrochloric acid with chlorine at 20°.

Cæsium plumbichloride, Cs_2PbCl_6, is easily obtained by treating a solution of lead chloride and excess of cæsium chloride with chlorine The salt is usually of a lemon colour, but is dark brown if prepared in the presence of strong hydrochloric acid and a large excess of lead chloride. The lemon-coloured salt crystallises in isolated octahedra; the brown salt in octahedric groups of octahedra.

E. C. R.

Ammonium Lead Haloïds. By H. L. WELLS and W. R. JOHNSTON (*Amer. J. Sci.*, **46**, 25—34).—A recent investigation (Abstr., 1892, 773) of the cæsium lead and potassium lead haloïds having established the existence of four very simple types of double salts, the authors re-investigated the ammonium lead haloïds, of which a considerable number, with very complicated formulæ, have been described. All of the extremely complicated ammonium lead salts were prepared by André (Abstr., 1883, 717, 903), and the authors are convinced that not one of the 11 salts described by him

exists. The authors' results show that the ammonium-lead haloïds are strictly analogous to the potassium salts. Their work has resulted in the preparation of the following series of salts :—

Type 2 : 1.	Type 1 : 1.	Type 1 : 2.
—	$3NH_4PbCl_3,H_2O$	$NH_4Pb_2Cl_5$
$(NH_4)_2PbBr_4,H_2O$	—	$NH_4Pb_2Br_5$
—	$NH_4PbI_3,2H_2O$	—

B. H. B.

Halogen Compounds of Potassium and Lead. By H. L. Wells (*Zeit. anorg. Chem.*, **4**, 346—351, and *Amer J. Sci.*, **46**, 190).—A compound, to which the author assigns the composition $K_2Pb_2I_8,4H_2O$, is precipitated from saturated solutions of potassium iodide containing iodine and lead iodide. It is stable on exposure to air, is decomposed by water and alcohol, and crystallises in lustrous, black prisms. The salt contains 16·5 per cent. of potassium iodide, but has not been obtained pure.

The *bromide*, $K_2Pb_2Br_8,4H_2O$, is obtained by adding bromine to a saturated solution of potassium bromide and lead bromide, and allowing the mixture to remain over night. It crystallises in dark brown prisms, is very unstable, and evolves bromine on exposure to air.

A stable, bright red salt is obtained in a similar manner from a solution containing free iodine and bromine in molecular proportions. It contains the halogens in the proportion 23Br : I.

The *salt*, $K_2Pb_2(BrI)_8,4H_2O$, is obtained by adding bromine to a concentrated solution of potassium iodide containing lead iodide. It crystallises in dark, bronze-coloured prisms. As both this salt and the iodide mentioned above crystallise in tetragonal prisms, the author assigns the above composition to the iodide. E. C. R.

Rubidium Lead Haloïds. By H. L. Wells (*Amer. J. Sci.*, **46**, 34—38).—The cæsium lead, potassium lead, and ammonium lead haloïds having been studied in the author's laboratory, an investigation of the rubidium salts has been made in order to make the work more complete. The salts prepared and described are : —

2 : 1-Rubidium lead chloride, $2Rb_2PbCl_4,H_2O$.
1 : 2-Rubidium lead chloride, $RbPb_2Cl_5$.
2 : 1-Rubidium lead bromide, $2Rb_2PbBr_4,H_2O$.
1 : 2-Rubidium lead bromide, $RbPb_2Br_5$.
1 : 1-Rubidium lead iodide, $RbPbI_3,2H_2O$.

B. H. B.

Dissociation of Calcium Plumbate. By H. Le Chatelier (*Compt. rend.*, **117**, 109—110).—The dissociation pressures of calcium plumbate at different temperatures are as follows :—

T°	880°.	940°.	950°.	1020°.	1060°.	1070°.	1100°.	1110°.
Pressure in mm.	47	112	117	350	557	570	940	1040

A higher temperature is required than in the case of barium peroxide, but, on the other hand, calcium plumbate has the advantage of

absorbing oxygen more rapidly, and, moreover, it does not require the moisture and carbonic anhydride to be removed from the air.

C. H. B.

Spectrum of Thallium. By H. Wilde (*Proc. Roy. Soc.*, **53**, 369—372).—Huggins observed a line in the spark spectrum of thallium to which he assigned the wave-length 6547 on Angström's scale; but the existence of this line was not confirmed by subsequent observers. The author shows that the line actually exists, but is almost coincident with the hydrogen line, C 6562, for which it has been mistaken. The real wave-length is λ6560, so that thallium has two well-marked lines, λ6560, 5349, corresponding with the lines of indium, λ4510, 4101, and gallium, λ4170, 4031. The spaces between the pairs of homologous lines increase with the atomic weight.

J. W.

Copper Fluorides. By Poulenc (*Compt. rend.*, **116**, 1446—1449).—The action of hydrofluoric acid on hydrated cuprous oxide yields metallic copper and a solution of cupric fluoride, and in this respect resembles the action of sulphuric acid on the same oxide.

Anhydrous cuprous fluoride, Cu_2F_2, can, however, be obtained by the action of hydrogen fluoride on cuprous chloride heated to dull redness. The action is not complete until the temperature is raised to 1100—1200°, the point at which cuprous fluoride volatilises. It can also be prepared by heating anhydrous cupric fluoride at 600° in a current of hydrogen fluoride, the temperature being raised to 1100—1200° towards the close of the operation.

Cuprous fluoride which has been fused is a ruby-red, transparent substance with a crystalline fracture. When exposed to the air, it is converted into cupric fluoride and becomes blue; in contact with water this change takes place more rapidly. It is insoluble in alcohol of 90°; dissolves in boiling hydrochloric acid, but is not, like cuprous chloride, precipitated when the solution is diluted. It is only slightly attacked by sulphuric acid, even when heated, but nitric acid acts on it with great energy, nitrogen oxides being evolved. When heated in presence of air, cuprous fluoride is converted into cupric oxide, and it is easily reduced by hydrogen at a red heat.

Cupric fluoride is obtained as a white, amorphous powder by the action of fused ammonium fluoride on the hydrated cupric fluoride, but this powder readily becomes crystalline when heated in hydrogen fluoride at 500°. The fluoride is also obtained directly in small, white crystals by heating cupric oxide, or hydrated cupric fluoride, at 400° in a current of hydrogen fluoride. If the temperature exceeds 500°, the compound is decomposed.

When exposed to air, the fluoride becomes blue owing to absorption of water, and it likewise becomes blue when placed in ether or alcohol which contains water. It is very readily dissolved by hydrochloric, nitric, and hydrofluoric acids, is very easily reduced by hydrogen, and when heated at 300° with exposure to air, it is completely converted into cupric oxide. Water vapour converts it into copper oxide and hydrogen fluoride; hydrogen sulphide converts it into cupric sulphide and hydrogen fluoride, and hydrogen chloride converts it into cupric chloride.

When heated above 500°, it yields cuprous fluoride, but no evidence of the evolution of free fluorine could be obtained. The dissociation is not complete below 1100—1200°. C. H. B.

Cuprous Phosphide. By A. GRANGER (*Compt. rend.*, **117**, 231—232).—When red phosphorus is immersed in an ammoniacal solution of copper sulphate, it becomes coated, as is well known, with a greyish deposit, which is a mixture of cuprous phosphide and metallic copper; the same occurs with an ammoniacal solution of copper phosphate, but the transformation is never complete, even at 100°. If, however, red phosphorus is heated with a large excess of copper phosphite and water in a sealed tube for four hours at 130°, its entire conversion is effected. The product is washed quickly with aqueous ammonia and water in succession, and dried in a vacuum. If the temperature has not exceeded that specified, it is not contaminated with metallic copper.

Cuprous phosphide, Cu_2P_2, is a grey powder resembling plumbago in appearance. It is attacked by chlorine and bromine in the cold, and is readily dissolved by dilute acetic acid; a mixture of it with potassium nitrate or chlorate detonates violently when struck. When heated in contact with air, it is oxidised to copper phosphate. It is decomposed by heat into products identical with those yielded by cupric phosphide (Abstr., 1892, 410). It is slightly soluble in hydrochloric acid, yielding a solution from which cuprous oxide is precipitated by potash, and which, when supersaturated with ammonia, precipitates metallic silver from an ammoniacal solution of silver nitrate. JN. W.

Simple Nature of Samarium. By E. DEMARÇAY (*Compt. rend.*, **117**, 163—164).—An examination of the absorption spectra of four samarium fractionations, prepared by Boisbaudran, gave practically identical results, the slight differences being due to the presence of traces of neodymium and erbium. The doubt thus cast on the hypothesis of the dual nature of samarium has been confirmed by a re-examination of the work leading to that hypothesis. The samarium band is resolved when the nitrate is examined with a sufficiently fine slit into two bands, $\lambda = 415$ and 419, and neodymium nitrate proves to exhibit a band of feeble, vague character, $\lambda =$ about 418, intermediate between these two. A variable percentage of neodymium in the samarium salt, together with a slit of varying width, are thus sufficient to account for the supposed variability of the samarium band, $\lambda = 415—419$. JN. W.

Samarium. By L. DE BOISBAUDRAN (*Compt. rend.*, **117**, 199—201; compare Abstr., 1892, 780).—The samarium bands vary in relative intensity with experimental conditions. Thus the band Z_ζ ($\lambda =$ 614·4—611·2) is strengthened relatively to the orange band by hydrochloric acid, and by other means, so that the increase in intensity of this band observed in the head fraction of an ammonia fractionation may have been due merely to change of conditions. A renewed examination of the head and middle fractions of this frac-

tionation showed a markedly diminished difference, which further successive fractionations with ammonia and oxalic acid failed to increase. In the head and tail fractions of the last fractionation, the band Z_ζ was, however, slightly less intense than in the middle fraction of the first fractionation.

An additional nebulous band in the green (wave-length of maximum intensity $\lambda = 535{\cdot}4$) is described; this is increased somewhat in intensity when the spark is very short, or when it impinges on the edge of the surface of the liquid instead of on the middle, and is also increased in intensity by acids. It is a little more intense in the head than in the middle fraction of the first ammonia fractionation. The most marked contrast it offers in behaviour to the band Z_ζ is that the latter is weakened or even obliterated by acetic acid. JN. W.

Manganous Sulphide. By U. ANTONY and P. DONNINI (*Gazzetta*, **23**, i, 560—567).—Manganous sulphide is thrown down from ammoniacal manganous solutions by ammonium sulphide as a pink precipitate, which the older workers supposed to be a hydrated sulphide; the authors show, however, that if it be collected, washed in an atmosphere of hydrogen sulphide, and dried at 70° in a current of carbonic anhydride, it has the composition MnS. The sulphide thus obtained consists of tiny, reddish, transparent crystals, and is contaminated with a little sulphur, which may be extracted by treatment with carbon bisulphide; its sp. gr. at 17°/17° is 3·55.

If the red precipitate be well washed, and left in a solution of ammonium sulphide for a few days, it turns green; the same change is also brought about by heating the red powder at 300—320°. The green modification is crystalline, and has the same composition as the red, but a somewhat higher sp. gr., namely, 3·63, referred to water at 17°. Neither modification loses sulphur on heating.

W. J. P.

Influence of Electricity on the Carburation of Iron by Cementation. By J. GARNIER (*Compt. rend.*, **16**, 1449—1451).—A bar of steel containing only 0·1 per cent. of carbon and a rod of gas carbon were placed end to end in a refractory tube, and well insulated. The tube was then heated at 900—1000°, and a current of 55 ampères and 7 volts was passed from the carbon to the steel. After three hours, it was found that that part of the iron opposed to the carbon cut glass easily, and a section showed that cementation had taken place to a depth of about 10 mm., whilst the carbon was corroded at the surface of contact.

Two bars of steel were then packed side by side in wood charcoal with a space of 10 mm. between them, and were heated at 900—1000° for three hours, a current of 55 ampères and 2·5 volts being passed from one to the other. It was found that the bar which served as the anode was practically unaffected, whilst in that which played the part of the cathode cementation had occurred to a considerable depth.

It would seem, therefore, that at about 1000° the cementation of iron

takes place with very great rapidity under the influence of a comparatively weak electric current. C. H. B.

Oxidation of Nickel Sulphide. By P. DE CLERMONT (*Compt. rend.*, **117**, 229—231).—When freshly precipitated, well-washed nickel sulphide is exposed to the air in a moist condition on filter paper, it gradually loses its moisture, and after 24 to 48 hours assumes an apple-green colour. The green product is extracted with water, and the insoluble residue dissolved in dilute hydrochloric acid. The acid solution is found to contain the basic sulphate $NiSO_4,6NiO$. The aqueous solution becomes greener on further exposure to the air, and is found to contain a mixture of the basic sulphate, the normal sulphate, and the sulphide, together with free sulphur.

When the sulphide is exposed under a layer of water several centimetres in depth, the oxidation proceeds more slowly, extending over months, whilst the relative amounts of the insoluble product and of basic sulphate in the latter are much diminished. Carbonic anhydride is also freely absorbed.

Since the sulphide dissolves in the sulphate (though only in the presence of sulphur) to form a stable compound, the oxidation of nickel sulphide is never complete under the conditions described above. Jn. W.

Potassium Tetrachromate and Ammonium Tetrachromate. By G. WYROUBOFF (*Bull. Soc. Chim.* [3], **9**, 156).—The author prepared and described in 1881 (*Bull. Soc. Min.*, **4**, 17) the potassium and ammonium tetrachromates obtained by G. C. Schmidt (compare this vol., ii, 16). J. B. T.

Chromopyrosulphuric acid. By A. RECOURA (*Compt. rend.*, **117**, 37—40 and 101—103).—When a solution containing 1 mol. of chromic sulphate and 5 mols. of sulphuric acid is evaporated on a water bath, a deep green, syrupy liquid is obtained, and if this is heated for one or two days at 110—115°, it solidifies in brittle, vitreous, transparent lamellæ, much paler in colour than the liquid. These crystals consist of *chromopyrosulphuric acid*, $(S_2O_7H)_4Cr_2(OH)_2$, derived from pyrosulphuric acid in the same way as chromosulphuric acid (this vol., ii, 470) is derived from sulphuric acid. It is very soluble in water, forming an opaline yellowish-green solution, very different in appearance from solutions of chromosulphuric acid, and this liquid has the remarkable property of yielding a flocculent, greenish-white precipitate, with solutions of any metallic salts, including those of sodium, potassium, and ammonium. Copper sulphate, for example, yields a greenish-white precipitate of the composition $CuCr_2 4SO_4$, but this, when boiled with a quantity of sodium hydroxide equivalent to the sulphuric acid that it contains, yields an insoluble green compound, which is copper chromite. The author concludes that in chromopyrosulphuric acid the hydroxyl groups are in direct union with the chromium, and the constitution of the copper salt is $(S_2O_7)_2Cr_2(O_2Cu)$. With alkali metals, the reaction is similar,

and in all cases 4 mols. of sulphuric acid are liberated, together with the acid in the precipitant, the general equation being

$$(S_2O_7H)_4Cr_2(OH)_2 + 2M'X' + 2H_2O = (S_2O_7)_2Cr_2(OM')_2 + 2HX + 4H_2SO_4.$$

All the precipitates are insoluble.

When solutions of alkalis are added to a solution of chromopyrosulphuric acid, a greenish-white precipitate forms, and the liquid becomes neutral when 10 equivalents of alkali have been added for each molecule of the salt. The alkali hydroxides yield the same precipitate as the corresponding salts, and the acid seems to be decabasic in consequence of the liberation of the 4 mols. sulphuric acid.

The salts $(S_2O_7)_2Cr_2(OM')_2$ are *pyrosulphochromites*.

Pyrosulphochromic Hydroxide.—If concentrated nitric, hydrochloric, or sulphuric acid is added to a solution of chromopyrosulphuric acid, a gelatinous greenish-white precipitate of pyrosulphochromic hydroxide is formed; this dissolves in pure water, and its solution precipitates all metallic salt solutions. The same product is obtained by heating chromopyrosulphuric acid at 140—150°, until it no longer loses weight. It is a slightly greenish, grey powder, and its solution is greenish-grey, and very opaline. It has already been shown that certain pyrosulphochromites yield chromites, and it is noteworthy how the association of chromous acid, $Cr_2O_2(OH)_2$, with the radicle S_2O_7 accentuates the acidic function of the hydroxyl groups.

It is remarkable that although pyrosulphochromic hydroxide, $(S_2O_7)_2Cr_2(OH)_2$, and chromosulphuric acid, $(SO_4)_2Cr_2(SO_4H)_2$, are isomeric, the salts of the former are all insoluble, whilst those of the latter are very soluble. The salts of the former are, however, converted into chromosulphates by prolonged boiling with water. The pyrosulphochromites yield chromites when treated with sodium hydroxide.

Chromopyrosulphuric acid loses 4 mols. SO_3 when heated at 140°, whereas chromotrisulphuric acid loses no SO_3 at 150°, and this fact agrees with the constitution already attributed to the former acid.

C. H. B.

Action of Gaseous Ammonia on Molybdenyl Chloride. By E. F. Smith and V. Lenher (*Zeit. anorg. Chem.*, **4**, 374—380).—A *compound* of the formula $Mo_3O_8N_3H_3$ is obtained by treating molybdenyl chloride, MoO_2Cl_2, with dry ammonia. Much heat is developed during the action, and ammonium chloride and water are formed. The compound has a black, metallic appearance, and is stable in the air; it does not combine with hydrochloric acid, but is energetically attacked by nitric acid (sp. gr. 1·42), slowly by dilute alkalis, and yields ammonia when fused with potassium hydroxide. When heated in an atmosphere of nitrogen, water is formed, and a red compound is obtained, which is probably molybdenum dioxide mixed with a small quantity of nitride. When treated with aqueous silver nitrate, crystals of metallic silver are deposited.

When molybdenyl chloride is heated to bright redness in an atmosphere of ammonia, an amorphous, black, metallic-looking mass is obtained, which has the composition $Mo_7O_{14}N_5H_{10}$. It is not attacked

by dilute alkalis, gives ammonia when fused with potassium hydroxide, is energetically converted into molybdic acid by the action of nitric acid, and precipitates silver from a solution of silver nitrate.

Other products have been obtained; their composition varies according to the time and temperature at which the action takes place. E. C. R.

Combination of Molybdates with Sulphurous acid. By E. PÉCHARD (*Compt. rend.*, **116**, 1441—1444).—In the absence of other inorganic acids, sulphurous acid does not reduce solutions of molybdates, but yields a series of complex compounds.

If sulphurous anhydride is passed into a warm and moderately concentrated solution of ammonium molybdate until the liquid smells strongly of the gas, *ammonium molybdosulphite*, $4(NH_4)_2O,10MoO_3,3SO_2 + 6H_2O$, separates in colourless, microscopic octahedra, which act on polarised light. It is readily decomposed by heat, both when solid and when in solution, and it is only slightly soluble in water.

Potassium molybdosulphite, $4K_2O,10MoO_3,3SO_2 + 10H_2O$, is obtained in a similar manner by passing sulphurous anhydride into a solution of potassium bimolybdate, prepared by the action of potassium carbonate on molybdic acid. It forms beautiful, amber-coloured, prismatic crystals, which lose water and sulphurous anhydride when heated. *Potassium ammonium molybdosulphite*, $4KNH_4O,10MoO_3,3SO_2 + 9H_2O$, is obtained by adding potassium bromide to a solution of ammonium molybdate previously saturated with sulphurous anhydride, and separates in long, yellow needles. It is only slightly soluble in water, and, when the solution is heated, sulphurous anhydride is given off, and potassium hydrogen molybdate separates.

When a solution of sodium hydrogen molybdate is saturated with sulphurous anhydride, and allowed to evaporate in a vacuum, it first deposits aggregations of lamellæ of the composition

$$4Na_2O,10MoO_3,3SO_2 + 12H_2O,$$

and afterwards colourless, very efflorescent octahedra of another hydrate, $4Na_2O,10MoO_3,3SO_2 + 16H_2O$.

Attempts to obtain the corresponding barium salt were unsuccessful. When barium chloride is added to a solution of one of the alkali salts, sulphurous anhydride is given off, and a white, crystalline precipitate separates, containing barium molybdosulphite and barium molybdate in proportions which vary with the conditions.

Selenious acid yields analogous, but much more stable, compounds, which will be described subsequently. C. H. B.

Combination of Selenious acid with Molybdates: Molybdoselenious acid. By E. PÉCHARD (*Compt. rend.*, **117**, 104—107).—When about one-fourth of its weight of selenious anhydride is added to ammonium molybdate in warm aqueous solution, the liquid, on cooling, deposits long, silky needles of the compound

$$10MoO_3,3SeO_2,4(NH_4)_2O + 4H_2O.$$

This salt is much more soluble in hot than in cold water, and is

insoluble in alcohol. When heated, it gives off water, ammonia, and selenious anhydride. Hydrochloric acid, when added to an aqueous solution, produces a gelatinous precipitate of ammonium hydrogen molybdoselenite, which dissolves with decomposition in excess of hydrochloric acid.

Potassium molybdoselenite is obtained by the action of selenious anhydride on potassium molybdate, and crystallises with $5H_2O$ in colourless, hexagonal tables. It is more soluble in water than the ammonium salt, and is slightly soluble in alcohol. When heated at 440°, it decomposes, with evolution of water and selenious anhydride. A double ammonium potassium salt can be obtained, and crystallises with $5H_2O$ in the same form as the potassium salt.

The sodium salt is analogous in composition, but crystallises with greater difficulty in very efflorescent octahedra containing $15H_2O$. It is very soluble in water, but insoluble in alcohol.

The barium salt is obtained by mixing hot solutions of barium chloride and one of the preceding salts; it separates, on cooling, in slender needles containing $3H_2O$. Lead molybdoselenite is white, and insoluble, even in hot water. The mercurous and silver salts, and the salts of other heavy metals, are amorphous and yellowish.

Molybdoselenious acid is obtained on decomposing the barium salt with sulphuric acid. It forms a yellow solution, which can be evaporated to a syrup, but will not crystallise.

Other compounds of molybdates with selenious acid exist, and the salt $5MoO_3,SeO_2,2(NH_4)_2O + 2H_2O$ has been obtained as a crystalline, white powder. C. H. B.

Action of Gaseous Ammonia on Tungstyl Chloride. By E. F. Smith and O. L. Shinn (*Zeit. anorg. Chem.*, **4**, 381—383).—Tungstyl chloride, WO_2Cl_2, is not attacked by dry ammonia at ordinary temperatures, but, on heating, a slow reaction sets in and a black mass is obtained, together with ammonium chloride and water. The compound has the composition $W_4O_4N_4H_2$. It is insoluble in water, is not attacked by hydrochloric acid or dilute alkalis, but is very energetically acted on by concentrated nitric acid, and yields ammonia when fused with potassium hydroxide. It is not altered by heating with concentrated sulphuric acid at 180—250°. When treated with aqueous silver nitrate, crystals of metallic silver are deposited.

E. C. R.

Tungstous Oxide associated with Colombous Oxide. By W. P. Headden (*Amer. J. Sci.*, **45**, 280—286).—In a paper on "Iron Tin Alloys" (this vol., ii, 211), the author referred to certain products as iron bottoms, the formation of which he discussed. This paper is a study of the residues obtained from those bottoms. In the residues, as obtained after having been freed from carbon, the author has found a mixture of columbous and tungstous oxides. Tungstous oxide, WO, as thus obtained, crystallises in the hexagonal system, mostly in hemiprisms having a light grey to tin-white colour, a metallic lustre, a hardness greater than glass, and a dark grey streak. The tungstous oxide was probably formed by the action of stannous oxide on metallic

tungsten, which had been reduced in the original tin charge of the furnace. B. H. B.

Volatilisation of Zirconia and Silica at a High Temperature, and their Reduction by Carbon. By H. Moissan (*Compt. rend.*, **116**, 1222—1224; compare this vol., ii, 507).—When zirconia is heated in an electric arc with a current of 360 ampères and 70 volts, it rapidly melts, and in about 10 minutes is in complete ebullition, giving off thick, white vapours, which condense to a white powder, consisting of opaque, microscopic granules; these scratch glass, and have all the other properties of zirconia; sp. gr. = 5·10. The residue in the crucible has a crystalline fracture, and dendritic crystals of zirconia are found in the cooler parts of the furnace.

If zirconia is fused in a carbon crucible under the conditions specified, there is found below the non-volatilised oxide a button of zirconium mixed with some zirconia, but free from carbon and nitrogen. If, on the other hand, the zirconia is mixed with excess of carbon, a zirconium carbide is obtained, containing from 4·22 to 5·10 per cent. of carbon. It has a metallic appearance and a brilliant fracture, and, when fused with excess of zirconia, yields pure zirconium, of sp. gr. 4·25, which scratches glass and rubies easily, and closely resembles the zirconium described by Troost. Zirconium carbides containing more than 5 per cent. of carbon inflame somewhat rapidly when exposed to the air.

Silica, in an arc of the same intensity, melts almost immediately, and is in complete ebullition after six or seven minutes. The vapours condense to a slightly bluish, white powder, consisting of a mixture of amorphous silica with small, opalescent spheres, which scratch glass easily; sp. gr. = 2·4. About 20 grams of silica can be volatilised in from 10 to 15 minutes, and the condensed product is very easily attacked by hydrofluoric acid and by alkalis.

Under the conditions specified, silica is reduced by carbon, and yields a crystalline silicon carbide, which is under investigation.

Small spherules of silica, identical in properties with those just described, are found on the inside of glass globes enclosing electric arc-lights. C. H. B.

Extraction of Zirconium and Thorium. By L. Troost (*Compt. rend.*, **116**, 1428—1429).—The volatilisation of silica in the electric arc (preceding abstract) can be utilised for the separation of silica from zirconia or thoria. Finely powdered zircon is intimately mixed with an excess of finely divided carbon, and compressed into small cylinders, which are placed in a carbon dish, and subjected to the action of an electric arc in a closed vessel through which a current of carbonic anhydride is passed. Silica volatilises very rapidly, together with a thick, black smoke, probably due to the reduction and volatilisation of silicon, which reoxidises outside the electric arc. When the volatilisation ceases, the residue contains only about 1·5 per cent. of silica, whereas the original zircon contains about 33 per cent.

Similar results are obtained with thorite and orangite, silicates of

thorium, and this preliminary separation of the silica greatly facilitates the isolation of the metal. C. H. B.

Arsenic Chlorosulphides and Antimony Chlorosulphides. By L. Ouvrard (*Compt. rend.*, **116**, 1516—1518).—Dry hydrogen sulphide acts on arsenic trichloride at the ordinary temperature, with evolution of hydrogen chloride and formation of a yellow precipitate, which, if the action is continued until the evolution of hydrogen chloride ceases, and the precipitate is washed with carbon bisulphide, consists partly of crystalline, and partly of amorphous, matter. The proportion of the latter varies, and it can be removed by levigation with carbon bisulphide. Both the amorphous and crystalline products consist of arsenic chlorosulphide, As_2S_3Cl. This compound is slowly decomposed by boiling water, with formation of arsenic trichloride and amorphous arsenious sulphide. It melts at about 120°, and volatilises at about 300° (out of contact with air), with decomposition into arsenic trichloride and sulphide.

If the hydrogen sulphide used in the preparation of the chlorosulphide is not quite dry, the product is simply the ordinary sulphide, and the same result follows if the reacting substances are heated.

Arsenious sulphide dissolves in the chloride when heated, but is deposited unchanged on cooling. If, however, a mixture of the two substances is heated in sealed tubes at 150°, the chloride being in excess, the compound AsS_2Cl is obtained in microscopic crystals, which melt and volatilise readily when heated out of contact with air. It is decomposed by water in the same way as the preceding compound, and is dissolved by solutions of ammonia and alkali carbonates.

If 1 part of the sulphide and 5 parts of the chloride are heated at 180° for 24 hours, and cooled slowly, the chlorosulphide, As_2S_3Cl, is obtained in very small, pale-yellow crystals.

Antimony trichloride, when treated at its melting point with a limited quantity of dry hydrogen sulphide, yields red-brown crystals of the chlorosulphide SbS_2Cl. It is insoluble in carbon bisulphide, melts readily, and is readily attacked by acids. If the passage of the hydrogen sulphide is continued until hydrogen chloride is no longer given off, the chlorosulphide Sb_2S_3Cl is obtained in small prisms. At a temperature above the melting point of the trichloride, the product of the action of hydrogen sulphide is the ordinary antimony trisulphide. C. H. B.

Arsenic and Antimony Iodosulphides. By L. Ouvrard (*Compt. rend.*, **117**, 107—109).—Dry hydrogen sulphide has no action on arsenic iodide in the cold, but at 200° some of the iodide volatilises, and a crystallised iodosulphide, As_2S_3I, remains. The compound $AsSI_2$ is obtained by heating together out of contact with air arsenic sulphide and excess of iodine, and crystallising the product from carbon bisulphide. If the arsenic sulphide is in excess, the product is the compound AsS_2I, described by Schneider.

A mixture of equal parts of iodine and precipitated antimony sulphide reacts at the ordinary temperature with development of

heat, and after treatment with carbon bisulphide, cinnabar-red needles of the compound SbS_2I are obtained. If 2 parts of iodine and 1 part of the sulphide are heated in a vacuous sealed tube, two products, SbS_2I and SbS_2I_3, are obtained, and can be separated by taking advantage of their different volatilities. Dry hydrogen sulphide acts readily on antimony iodide at about 150°, and yields reddish-brown crystals of the compound SbS_2I. C. H. B.

Metallurgy of Bismuth. By E. Matthey (*Proc. Roy. Soc.*, **52**, 467—472; compare Abstr., 1891, 1161).—The purification of bismuth from arsenic has hitherto been accomplished by fusing it with iron in presence of a flux, the compound of iron and arsenic being then removed as a scum; the method requires considerable time, and involves a serious loss of bismuth by volatilisation. The author finds that the whole of the arsenic can be eliminated by exposing the well stirred alloy, when heated above its melting point, to the action of air. No loss of bismuth occurs. In one experiment, 700—800 kilos. of alloy, containing 0·65 per cent. of arsenic, and melting at 278°, gave up the whole of the arsenic on heating at 395—513°. On heating the alloy in a vacuum, the arsenic is volatilised at about the same temperature as when heated in air.

Bismuth may also be completely freed from antimony by prolonged fusion and constant stirring, the antimony oxidising and separating as an oily film; in one experiment an alloy containing 0·80 per cent. of antimony, together with other impurities, was heated for five hours at 350°, and afterwards during about four hours at 458°; a slight loss of bismuth occurs. The above temperatures were determined by means of Le Chatelier's platinum-rhodium pyrometer. J. B. T.

Gold Crystals containing Mercury. By T. Wilm (*Zeit. anorg. Chem.*, **4**, 325—334).—If gold in the form of small reguli, or as a fine powder, is dissolved in mercury under water in such quantities that the amalgam is quite liquid, then warmed for some time on the water-bath, and the amalgam treated with strong nitric acid as long as mercury is dissolved, the gold is recovered as a yellowish-brown powder, which is not crystalline, and contains mercury which cannot be removed by treatment with nitric acid, but is easily expelled by heat.

If in the place of mercury a dilute liquid amalgam of sodium is employed under water, the gold is recovered in bright-yellow, lustrous prisms or needles 2—3 mm. in length. The crystals contain from 5·45 to 11·45 per cent. of mercury, which cannot be entirely removed by boiling with strong nitric acid. When heated, the mercury is expelled, and the gold is obtained in dark coloured cakes, showing its former crystalline texture.

After the dissolution of the gold in the sodium amalgam, the aqueous liquid becomes rose-red, and finally dark-violet. If the mixture of gold amalgam and water is warmed on the water-bath, a bluish-green solution is obtained. These solutions may be exposed to the air at ordinary temperatures without any alteration in colour taking place. When acidified with hydrochloric acid, a black precipitate of pure gold is obtained. The black gold differs from the

ordinary modification in its extreme lightness; also it is soluble in alkaline solutions, and does not amalgamate with mercury or with sodium amalgam. When heated, it yields the ordinary modification as a violet-red powder. E. C. R.

Mineralogical Chemistry.

Three supposed New Sulphides of Iron and Nickel. By S. L. PENFIELD (*Amer. J. Sci.*, **45**, 494—497).—The author brings forward evidence to show that folgerite, blueite, and whartonite, sulphides of iron and nickel from the Sudbury nickel mines, Ontario, Canada, described by S. H. Emmens, cannot be regarded as distinct species. It is clear that little dependence can be placed on formulæ deduced from analyses of minerals of such doubtful purity, especially where a chief constituent is determined by difference. B. H. B.

Deposits of Native Soda near Laramie, Wyoming. By H. PEMBERTON, Jun., and G. P. TUCKER (*Chem. News*, **68**, 19—20).—Deposits of sodium sulphate, generally known as the Union Pacific Lakes, are found in a nearly rainless region on the high Wyoming plateau, in the neighbourhood of the town of Laramie. The lower and greater portion of these deposits is of uncertain thickness, and is known as the "solid soda;" it consists of a mass of crystals of a faint greenish colour, mixed with a considerable amount of black, slimy mud; its composition is Na_2SO_4, 36 per cent.; $CaSO_4$, 1·45 per cent.; $MgCl_2$, 0·77 per cent.; NaCl, 0·21 per cent.; H_2O, 46·87 per cent.; insoluble residue, 13·86 per cent. The upper portion of the deposits, from 3 to 12 inches thick, is formed by solution from the upper layers of the lower part, and the subsequent evaporation or cooling of the solution; it has the following composition (calculated as anhydrous), Na_2SO_4, 99·73, and $MgCl_2$, 0·26, per cent., with a trace of insoluble matter; the article manufactured in Laramie is, however, not so pure.

Samples of the supernatant water taken from some of these "lakes" or deposits at a time when they were entirely under water gave the following numbers, in grams per litre, on analysis.

	Big Lake.	Track Lake.	Red Lake.
Sp. gr.	1·0487	1·0725	1·0887
Na_2SO_4	44·90	75·63	93·07
CaSO	1·75	1·46	2·01
MgSO	0·60	0·70	1·43
$MgCl_2$	6·43	3·00	4·16
$Na_2B_4O_7$ (?)	1·46	1·21	0·75
Total solids	55·14	82·00	101·42

The borax represents the results of titration with standard acid using methyl orange as indicator. Samples from two other lakes,

yielded a residue which, when calcined, contained only 43·12 and 69·55 per cent. of sodium sulphate, besides magnesium and calcium sulphates and insoluble matter. D. A. L.

Ettringite from Tombstone, Arizona. By A. J. Moses (*Amer. J. Sci.*, **45**, 489—492).—The author has examined several specimens of ettringite from the Lucky Cuss mine, Tombstone, Arizona. The mineral occurs in white, radiating fibres; it has a sp. gr. of 1·55, and fuses readily before the blowpipe. It thus differs from Lehmann's ettringite in that the latter occurs in acicular, hexagonal crystals, has a sp. gr. of 1·75, and is said to be infusible. Analysis gives results corresponding with the formula $(H_{22}Ca_{10}Al_4)O_{30}(SO_3)_5 + 40H_2O$. This formula suits not only the analysis of the Arizona mineral almost exactly, but also that of the Ettringen variety described by Lehmann, at least as well as the formula given by him. The analytical results were as follows.

	CaO.	Al_2O_3.	SO_3.	H_2O.
I	27·27	7·76	19·15	45·82
II	26·31	9·72	18·54	45·41

I, ettringite from Ettringen; II, ettringite from Arizona.

It may, therefore, be concluded that this mineral is to be placed in a group of hydrous basic sulphates of the general formula $2R_2O_3,SO_3 + nH_2O$. This group is composed of—

Glockerite.....		$2Fe_2O_3,SO_3 + 6H_2O$
Felsöbanyite.....		$2Al_2O_3,SO_3 + 10H_2O$
Paraluminite.....		$2Al_2O_3,SO_3 + 5H_2O$
Ettringite.	Arizona	$2[H_2,CaAl_2O_3]SO_3 + 8H_2O$
	Ettringen ..	$2[H_2CaAl_2O_3]SO_3 + 8H_2O$

B. H. B.

Formation of Natural Aluminium and Iron Phosphates. By A. Gautier (*Compt. rend.*, **116**, 1491—1496).—Minervite, $Al_2(PO_4)_2 + 7H_2O$ (this vol., ii, 419), is formed by the action of ammonium phosphate, derived from a bed of guano, on an underlying layer of hydrargilite, and the aluminium phosphates in the guano islands Alta Vala, Redonda, and Commandeur have been formed in the same way. Minervite can, in fact, be obtained artificially by allowing a mixture of gelatinous aluminium hydroxide and a solution of twice its weight of ordinary ammonium phosphate to evaporate to dryness at 30°, washing in water, dissolving in hydrochloric acid, and precipitating in the cold with an excess of sodium acetate. In separates in small, short prisms and in triangular lamellæ.

Clay is slightly attacked by ammonium phosphate at about 85°, but calcium hydrogen phosphate seems to be without action on it. Similar changes take place in soils, and minute quantities of aluminium phosphate can be extracted from some soils by means of dilute solutions of alkalis.

Aluminium phosphate is slightly soluble in an ammoniacal solution of ammonium phosphate, and still more soluble in an ammoniacal solution of ammonium lactate. The latter is a product of bacteroidal

fermentation, and the fact that aluminium phosphate is soluble in the products of the fermentation of manures and soils probably has great influence on the assimilation of this compound by plants.

In contact with ferrous carbonate in fine powder, or in solution in water containing carbonic anhydride, ammonium phosphate very slowly produces ferrous phosphate. If the two substances are heated at 83° for a long time, the phosphate $Fe_3(PO_4)_2 + 6H_2O$ is formed in microscopic, acicular crystals, the composition of which differs but slightly from that of the purest varieties of vivianite, $Fe_3(PO_4)_2 + 8H_2O$.

The putrefactive decay of fish, molluscs, &c., results in the production of ammonia, together with hydrogen sulphide and hydrogen phosphide. In the case of the more stable parts, such as bone, chitinous envelopes, hair, &c., these changes, although slow, continue for a long time. For months, and even years, the change proceeds, and the substances remain distinctly alkaline. When water containing calcium and iron carbonates, calcium phosphate, &c., comes into contact with the decaying substances, precipitation takes place. Ferrous sulphide is one of the products, and by the subsequent action of hydrogen sulphide and air it becomes converted into pyrites, thus, $FeS + SH_2 + O = FeS_2 + H_2O$. Pyrites may also be formed directly by the action of hydrogen sulphide on ferrous carbonate in presence of oxygen, thus, $FeCO_3 + 2SH_2 + O = FeS_2 + 2H_2O + CO_2$. When once pyrites has been formed, it remains, by reason of its insolubility, and forms a nucleus for the deposition of a further quantity. Any calcium or aluminium phosphate, calcium or iron carbonates, &c., which may have been deposited in the decaying substance, may possibly be removed again by the solvent action of water charged with carbonic anhydride and with salts, other substances taking their place. There will, however, always be a tendency towards the accumulation of the less soluble of the substances deposited. Where, for instance, the fossil is subjected to the prolonged action of water, it may be that only silica will be left.

C. H. B.

Kehoeite, a New Phosphate from Dakota. By W. P. HEADDEN (*Amer. J. Sci.*, **46**, 22—25). This mineral forms seams and bunches in an argentiferous galena carrying zinc blende and iron pyrites, at the Merritt mine, near Galena, South Dakota. Analysis gives results corresponding with the formula $R_3P_2O_8 + 2Al_2(OH)_6 + 21H_2O$, in which $R = Zn_4 + Ca_4$. The mineral is named after the gentleman who first observed its occurrence. B. H. B.

Xenotime from El Paso Co., Colorado. By S. L. PENFIELD (*Amer. J. Sci.*, **45**, 398—399).—The occurrence of this mineral from the tysonite and bastnaesite locality of El Paso Co. has already been noted by W. E. Hidden (Abstr., 1885, 878). An analysis of 0·2 gram of a second crystal gave the following results.

P_2O_5.	$(YtEr)_2O_3$.	Ignition.	Total.
32·11	67·78	0·18	100·07

The mineral is thus a normal phosphate. Its sp. gr. is 5·106.

B. H. B.

Rose-coloured Lime- and Alumina-bearing Talc. By W. H. Hobbs (*Amer. J. Sci.*, **45**, 404—407).—The mineral described was met with in the Adam Quarry, near Canaan, Connecticut, enclosed in white crystalline dolomite. Analysis shows that the mineral is a normal talc, in which the magnesia is in part replaced by lime, and the silica by alumina. The trace of manganese observed accounts for the rose colour, which disappears when the mineral is exposed to sunlight. The analytical results were as follows.

SiO_2.	Al_2O_3.	MgO.	CaO.	FeO.	MnO.	H_2O.	Total.
61·48	3·04	25·54	4·19	0·77	trace	5·54	100·56

The mineral is shown to belong to the talc family by its chemical composition as well as by its physical and optical properties. That it is a distinct variety is shown by its high percentages of lime and alumina, by its low fusibility and easy decomposability by acids, and by its exceptional rose colour. B. H. B.

Zunyite from Colorado. By S. L. Penfield (*Amer. J. Sci.*, **45**, 397—398).—This mineral was first described by W. F. Hillebrand in 1884 from the Zuñi mine, near Silverton, Colorado. It is interesting to know that a second locality for this rare mineral has been found at the Charter Oak mine, near the town of Red Mountain, about 5 miles north of the original locality. The zunyite crystals occur in a porphyrite, much altered by steam and fumerole action. Analysis gave results corresponding with the formula $[Al(Cl,F,OH)_2]_6Al_2Si_3O_{12}$, the agreement between the author's and Hillebrand's analyses being very satisfactory. Zunyite also occurs at the same mine in a pulverulent form resembling kaolin. B. H. B.

Cookeite from Paris and Hebron, Maine. By S. L. Penfield (*Amer. J. Sci.*, **45**, 393—396).—Excellent specimens of the mineral cookeite, first described by G. J. Brush in 1866, have been obtained from Paris and Hebron. Cookeite is related to the chlorites and micas, having a distinct basal cleavage, and crystallising, like them, in the monoclinic system. Analysis gave results corresponding with the formula $H_{12}Li_2Al_6Si_4O_{24}$, or simplified to that of a basic metasilicate, $Li[Al(OH_2)]_2Si_2O_6$. The sp. gr. of the mineral is 2·67.

B. H. B.

Sodalite-syenite from Montana. By W. Lindgren (*Amer. J. Sci.*, **45**, 286—297).—The author describes a series of specimens, in the United States National Museum, collected in the northern part of Montana. Descriptions and analyses are given of the following rocks: (1) Porphyrites and quartz-porphyrites from the Moccasin Mountains. They are intrusive holocrystalline rocks of post-Cretaceous age, and consist of quartz, orthoclase, soda-lime, felspar, and hornblende. (2) Porphyritic, dark-coloured post-Cretaceous dyke rocks from the Bear Paw Mountains. They consist of augite, olivine, biotite, and triclinic felspar, and have a general resemblance to the lamprophyric dyke rocks of Rosenbusch. (3) A post-Cretaceous sodalite-syenite from Square Butte. This rock consists of hornblende, orthoclase, albite, sodalite (8 per cent.), and analcime. No nepheline

is found; but the interstitial analcime, of which there is 3 per cent., might possibly have been derived from that mineral. B. H. B.

Basic Dyke thought to contain Leucite. By J. F. KEMP (*Amer. J. Sci.*, **45**, 298—305).—In 1888 the author examined the elæolite-syenite of Beemerville, New Jersey. Since the paper describing his investigations was published, several descriptions have appeared of elæolite-syenite districts elsewhere, and in particular of the basic rocks associated with them, so that basic dykes are now recognised as invariable attendants on this form of plutonic rock. The author now describes a basic dyke, near Hamburg, not far from Beemerville, in New Jersey. The spheroïdal inclusions offer the point of chief interest, as they have been thought to indicate leucite. Analysis shows that they are practically analcime. Assuming a change from leucite, it is necessary to account for a large accession of soda, and as regards the corresponding alteration from nepheline, a much smaller accession of potash. Although it is impossible to settle the question without the discovery of perfectly fresh material, either of nepheline or of leucite, in the spheroïds, the analytical results rather favour original nepheline than original leucite.

B. H. B.

Volcanic Rocks from Gough's Island, South Atlantic. By L. V. PIRSSON (*Amer J. Sci.*, **45**, 380—384).—These rocks were gathered as beech pebbles from the shore of Gough's Island, by the captain of a whaling vessel. Nothing has been published on the geology of this remote region. All the pebbles represent very fresh volcanic rocks which may be referred to trachytes or to basalts. Basalt is represented by two varieties, one of which is a rock of dark-grey colour thickly dotted with black augite, yellow olivine, and white felspar. The second type is of a dark greyish-brown colour, exhibiting in thin sections iron ore, apatite, olivine, augite, and felspars. It contains 49·55 per cent. of silica, and its sp. gr. is 2·643. Trachyte is represented by trachytic tuffs and obsidian. The latter gave on analysis 61·22 per cent. of silica, 1·88 of lime, and 0·44 of magnesia, whilst the percentage of soda was 6·49 and that of potash 5·93. The glass, therefore, is to be referred to trachyte, perhaps of the phonolithoïd type. The analyses of these rocks are of interest in establishing the recent volcanic nature of this solitary island.

B. H. B.

Physiological Chemistry.

Nutritive Value of Albumoses. By H. HILDEBRANDT (*Zeit. physiol. Chem.*, **18**, 180—192).—Careful experiments on metabolic exchanges when albumoses are administered, given with full details, confirm the already well known fact that these substances have a high nutritive value. W. D. H.

Nutritive Value of Proteïds. By E. KRAUSS (*Zeit. physiol. Chem.*, **18**, 167—179).—In considering the metabolic value of proteïd food, it is not merely enough to put down the intake and output of nitrogen. A third factor is the amount of nitrogenous substance which undergoes putrefactive change in the intestine forming indole, &c., which, so far as the economy is concerned, is a waste. The amount of this waste can be estimated by the indican of the urine, or by the estimation of the ethereal hydrogen sulphates in the same secretion. This has recently been insisted on by Winternitz (Abstr., 1892, 1116), who made his experiments with milk, and attributes to lactose a power of lessening putrefactive change. Hirschler (Abstr., 1886, 729) regards carbohydrates as valuable antiseptics in the organism. The present experiments, performed with meat and with meat and bread diets, fully confirm this view. W. D. H.

Proteïd in Diet. By F. HIRSCHFELD (*Chem. Centr.*, 1893, i, 790—791; from *Berl. klin. Woch.*, **30**, 324—329).—Attention is called to former work (Abstr., 1889, 174) in which it is shown that less proteïd is compatible with health than was formerly supposed; and to the importance of this fact in the construction of dietaries. It is further pointed out that merely chemical analysis of a food does not form a criterion of its nutritive value. Other factors, such as weight, volume, and digestibility, must be taken into account.

W. D. H.

Influence of Tea and Coffee on Artificial Digestion. By C. SCHULTZ-SCHULTZENSTEIN (*Zeit. physiol. Chem.*, **18**, 131—132).—The few experiments given show that infusions of tea and coffee, when mixed with an artificial gastric digestion in amounts approximately equal to that which would occur in the stomach after a meal accompanied by tea or coffee, impede digestion. The amount digested without such addition being 94 per cent., that in the specimens mixed with tea and coffee varied from 61 to 68 per cent. W. D. H.

Occurrence of Hydrochloric acid in the Stomach. By F. MARTIUS (*Chem. Centr.*, 1893, i, 856).—Hydrochloric acid is rapidly secreted by the stomach, and five minutes after food has been taken it is already quantitatively detectable. Unless acids have been present in the food, the total acidity of the stomach may be taken as due to hydrochloric acid. But the acid forms a compound with the albumin of the food and so becomes indifferent towards vegetable colours.

Organic acids, and lactic acid in particular, are only secreted in amount sufficient to affect the acidity of the stomach under pathological conditions. L. DE K.

Gases of Blood during Anæsthesia. By T. OLIVER and F. C. GARRETT (*Brit. Med. J.*, 1893, ii, 683—684).—A preliminary note on the gases of the blood during anæsthesia with chloroform, ether, methylenic dichloride, and nitrous oxide, the experiments being performed on dogs and rabbits; the most striking fact noted was a remarkable rise in the percentage of nitrogen in the blood.

W. D. H.

Chlorosis. By E. L. Jones (*Brit. Med. J.*, 1893, ii, 670—672).—From the study of the specific gravity of the blood and serum at various ages in the two sexes, the theory is advanced that chlorosis is an exaggeration of what always occurs in women at puberty, a fall in hæmoglobin and specific gravity. In the male, the opposite takes place, and they do not suffer from the disease. The connection between chlorosis and gastro-intestinal congestion is also pointed out, but the relationship is not explained. W. D. H.

Intravascular Coagulation. By W. D. Halliburton and T. G. Brodie (*Brit. Med. J.*, 1893, ii, 682).—Analysis has shown that the proteïd obtainable from various cellular organs by admixture with sodium chloride, in a method already described (this vol., ii, 133), is a nucleo-albumin, and thus resembles Wooldridge's tissue fibrinogen. The physiological effect of the two substances is also identical, leading to intravascular clotting, chiefly in the venous, but also sometimes on the arterial side of the circulation. Death occurs from stoppage of the respiration, and the fact that severance of the vagi makes no difference in the experimental result points to the cause of death in the respiratory centre. The toxic material may be conveniently dried in a vacuum at a low temperature, and dissolved for use in dilute sodium carbonate solution. Such solutions are clear, somewhat viscous, and free from lecithin. Even when kept antiseptic with thymol, they lose their power after some days, and a curious change noticed was that after some weeks they became pink, and subsequently red. The spectroscope reveals no bands.

The use of nucleo-albumin to produce clotting in hæmorrhages, or aneurisms, cannot be recommended, as the substance is so deadly. Sir Joseph Fayrer (see next abstract) and others have pointed out that intravascular coagulation is by no means an infrequent cause of death, and it can hardly be doubted that the poisonous substance here also is a nucleo-albumin. W. D. H.

Cardiac and Pulmonary Thrombosis. By J. Fayrer (*Brit. Med. J.*, 1893, ii, 682—683).—Clinical details of two cases are given. W. D. H.

Glycogen in Blood and Pus. By Huppert (*Zeit. physiol. Chem.*, **18**, 144—166; compare this vol., ii, 176).—Full details are given of the experiments on which the author rests his conclusions. The leucocytes in the blood are probably the source of the glycogen found. W. D. H.

Influence of Fever on Hepatic Glycogen. By D. Noël Paton (*Brit. Med. J.*, 1893, ii, 682).—Since it is the disintegration of proteïds, and not of fats and carbohydrates, which characterises the metabolism of fever, it is important to investigate the effect of that condition on the glycogen of the liver. In the experiments, pairs of young rabbits were kept on the same diet, and weighed daily for considerable periods, thus rendering the hepatic glycogen fairly uniform. By diminishing the heat elimination by placing one of the pair in a hot chamber, the body temperature rose, and on killing it the glycogen was markedly diminished, as compared with that in the other

rabbit. At the same time, the reducing substances of the blood and liver were increased, probably indicating sugar formed from the glycogen. Pyrexia, produced by toxic products (yeast culture), led to corresponding results. The effect may be partly explained also by diminished formation of glycogen. W. D. H.

The Work of the Kidney. By W. H. Thompson (*Brit. Med. J.*, 1893, ii, 681).—The experiments were made on dogs, and the urine collected by cannulæ in the ureters. 1·5 to 2 milligrams of atropine, and in other cases 3 to 4 milligrams of morphine, per kilo. of body weight were given intravenously. The results were, that the urine was diminished, and urea also was diminished; the nitrogen, other than that in urea, was increased. These results could not be explained as the result of interference with blood pressure, but taken with the fact that heat is produced in the kidney during its performance of work, tends to the belief that some of the urea is formed in the kidney itself out of one or more of the other nitrogenous compounds, and that this process of true secretion is lessened by the drugs which produce similar effects in other glands. W. D. H.

Carbohydrates of Normal Urine. By K. Baisch (*Zeit. physiol. Chem.*, **18**, 193—206).—The investigations of the older chemists showed that the presence of a reducing substance, presumably sugar, was constant in normal urine. It was not, however, until Baumann's benzoic chloride method was introduced that it became possible to isolate this substance and to study its properties, and even now the matter is far from settled, Wedenski having shown that the carbohydrates are probably two in number, and that the benzoyl compound contains small quantities of nitrogen (Abstr., 1889, 293). The present research relates mainly to the preparation and properties of the benzoyl compound. Future papers are promised on the varieties of carbohydrate which can be obtained from it. It is, however, briefly stated that the properties of one of these corresponds closely to those of dextrose.

The best proportions of reagents to use are 40 c.c. of benzoic chloride, 400 c.c. of sodium hydroxide, and a litre of urine. Other proportions give a smaller yield with a larger amount of ash; the ash consists chiefly of magnesium phosphate, which can be removed by means of dilute hydrochloric acid. But in all cases there is from 1 to 2 per cent. of nitrogen. Similar results followed if the urine had been previously treated with normal or basic lead acetate. The melting point varied in different preparations from 95° to 130°; the carbon from 66·5 to 67·7, the hydrogen from 5·15 to 5·57.

W. D. H.

Episarkine. By G. Salomon (*Zeit. physiol. Chem.*, **18**, 207—212). Balke (this vol., i, 536) has recently described under this name a new xanthine-like compound in the urine. It appears to be identical with a substance of hitherto doubtful nature, described by the author at various times, in the urine of the pig and ox, and in the urine of leucæmic patients. Further details are promised.

By the solubilities of their silver compounds in hot nitric acid, the

xanthine-like substances of the urine may be divided into the hypoxanthine fraction, including hypoxanthine, guanine, carnine, adenine, and episarkine, and the xanthine fraction, which includes xanthine, paraxanthine, and heteroxanthine. W. D. H.

Diabetic Coma. By V. HARLEY (*Brit. Med. J.*, 1893, ii, 666—669).—Coma can be produced in dogs by the introduction of sugar into the circulation, the ureters being tied. The comatose stage is preceded by a convulsive one. This is not simply due to the ligature of the ureters, nor is it due to the sugar, which diminishes in the blood as the symptoms appear. It is due to toxic substances produced from the sugar. Alcohol and acetone were found, and these may be partly the cause of the diminished oxidation which experiments on the gaseous interchanges show. Coma is, however, principally due to acid products which combine with the carbonates and ammonia of the blood, thus hindering that fluid from carrying carbonic anhydride to the lungs for elimination. There is at the same time a diminution in the oxygen absorbed. β-Hydroxybutyric acid is not formed. W D. H.

Amount of Lecithin in Butter. By E. WRAMPELMEYER (*Landw. Versuchs-Stat.*, **42**, 437—438).—The ash from 100 grams of butter yielded 0·04512 gram of phosphoric acid, whilst margarin gave only 0·0160 gram. Analyses made with filtered fat showed that the ash of margarin treated in this manner contained practically no phosphoric acid, whilst the ash of butter was found to contain much reduced and very variable quantities. The average amount of lecithin calculated on the total phosphoric acid now found was 0·017 per cent. (Beilstein, 2 Ed., **1**, 334, gives 0·15—0·17 per cent.). The results of analyses of seven samples is given in a table, which shows also the melting and solidifying points of the butters, and the amounts of volatile fatty acids. N. H. M.

Influence of Chloral Hydrate and Amylene Hydrate on Metabolism. By E. HARNACK and J. REMERTZ (*Chem. Centr.*, 1893, i, 841—842; from *Fortsch. d. Med.*, **11**, 265—270).—The experiments were tried on dogs. The sulphur in dog's urine is in four conditions, and not in three, as in human urine. These are A, as ordinary sulphates; B as ethereal hydrogen sulphates; C, as thiosulphates (absent in human urine); and D, as organic sulphur compounds. Chloral hydrate increases the output of sulphur by 18 per cent.; this is due to increase of B and D. Amylene hydrate lessens the total output of sulphur, as it depresses the oxidation processes in the organism. Chloral hydrate diminishes the excretion of urea during the first two days of its administration, and increases it subsequently. The total nitrogen runs the same course, but the effect is not merely due to urea, but also to organic compounds which contain sulphur in addition. This is due to increased metabolism of tissue proteïd, rather than to an increase of oxidation processes. The chloral itself leads to an increase of urinary chlorides. Amylene hydrate lessens the output of nitrogen and urea. Both hypnotics lessen oxidation, and

lower the body temperature. This action appears to be independent of their narcotic and paralytic effects, which are due rather to the alkyl than to the halogen. W. D. H

Physiological Action of Pyridine and Naphthalene Derivatives. By R. Cohn (*Zeit. physiol. Chem.*, **18**, 112—130).—His (*Arch. exp. Path. Pharm.*, **22**) found that pyridine leaves the body in the urine as methylpyridylammonium hydroxide, $C_5NH_5Me{\cdot}OH$; as this investigation was made previous to the publication of Ladenburg's (*Annalen*, **247**, 1) method of preparing pure pyridine, and as the result is unique in animal chemistry, it was thought advisable to repeat the experiments. The results obtained by His were completely confirmed by those of the present research. Attempts to obtain pyridine aldehyde by Ladenburg's method from α-picoline having failed, the action of α-picoline itself on the body was investigated; this substance was found to leave the body as a glycocine compound of α-pyridinecarboxylic acid, to which the name *α-pyridinuric acid* is given.

Nencki states that naphthalenecarboxylic acid leaves the body in the urine unchanged (*Arch. exp. Path. Pharm.*, **30**, 302); this was put to the test. It was found that in rabbits the α-acid is excreted unchanged, but the β-acid leaves the body as the glycocine compound, β-naphthuric acid. In dogs, the β-acid is excreted unchanged, while the α-acid leaves the body as α-naphthuric acid. W. D. H.

A complete Process of Reduction occurring in the Animal Tissues. By R. Cohn (*Zeit. physiol. Chem.*, **18**, 133—136).—The author has previously shown (Abstr., 1892, 1504) that in rabbits metanitrobenzaldehyde leaves the body in the urine as acetylamidobenzoic acid. This involves three changes: 1st, an oxidation of the aldehyde group to a carboxyl group; 2nd, a reduction of the nitro-group to an amido-group; and, 3rd, a synthesis with acetic acid, water being eliminated. In the dog, this does not occur, and the shortness of its alimentary canal was regarded as the probable explanation of the difference. But the present experiments show that this cannot be correct, as the reduction occurs in the tissues after subcutaneous injection; indeed, more of the reduction product is then obtained in the urine than when the drug is given in the usual way. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Nitrification. By E. Godlewski (*Forsch. a. d. Gebiete d. Agrik. physik.*, **16**, 240—242: from *Anzeiger d. Akad. d. Wissens. Krakau*, 1892).—According to Winogradsky, both the nitrite and the nitrate organisms have the power of vegetating in solutions absolutely free from organic matter, as, for instance, a solution containing ammonium

sulphate and potassium phosphate, with addition of basic magnesium carbonate, and he concludes that the organisms derive their carbon from the magnesium carbonate. This view was opposed by Elfving (*Forsch. Geb. Agrik. phys.*, **14**, 304), who considered it more probable that the organisms derived their carbon from volatile compounds absorbed from the air. The following experiment was made by the author.

Four Erlenmeyer flasks, each containing water (100 c.c.), ammonium sulphate (0·05 gram), potassium phosphate (0·1 gram), and magnesium carbonate (1 gram), and seeded with 1 drop of a nitrifying organism cultivation, were kept under the following conditions. No. 1 was closed with cotton wool; Nos. 2, 3, and 4 were placed on glass dishes and covered with bell jars, which were closed below with potash, sulphuric acid, and a permanganate solution respectively. In the flask exposed to air, nitrification was vigorous; in those kept over sulphuric acid and over permanganate, it was also vigorous, but somewhat slower; whilst in the flask kept over potash, there was no nitrification at all. The experiment was repeated with the same result. It is concluded that the organisms derived their carbon from the carbonic anhydride of the air or of the double carbonate.

In a second series of experiments, in which known amounts of ordinary air, or air containing large amounts of carbonic anhydride, were employed, it was found that the carbonic anhydride actually did nourish the micro-organisms. The nitrogen of the air increased, showing that in the process of nitrification a portion of the nitrogen of the ammonia is liberated. N. H. M.

Changes in Mouldy Bread. By A. Hebebrand (*Landw. Versuchs-Stat.*, **32**, 421—427).—Samples of rye bread were infected from mouldy bread, and kept for periods of 7 and 14 days, similar samples being at once dried for analysis. The mould was chiefly *Penicillium glaucum* and *Mucor mucedo*. The results showed that there was a considerable loss of substance under the influence of mould, mainly owing to the conversion of the carbohydrates into carbonic anhydride and water. The fat and crude fibre increased in amount, whilst, although there was only a slight loss of proteïd matter, the loss of carbohydrates caused the percentage of proteïds to be much higher in the dry substance of the mouldy bread. The decomposition of proteïds caused an increase in the amount of amides. In a subsequent experiment, the bread (47·65 grams) was first sterilised, and then seeded with a pure cultivation of *Penicillium glaucum*. The carbonic anhydride evolved was determined, and it was found that it amounted to about 21·5 milligrams per hour. At the conclusion of the experiment, the flask containing the bread was heated in a glycerol bath, and the distillate collected. This had an odour of fresh cider refuse, and was strongly acid; it contained no alcohol. The bread had lost 18·69 per cent. of its weight of dry substance. The following numbers show the percentage composition (1) of the dried fresh bread and (2) of the dried mouldy bread.

	Crude proteïn.	Pure proteïn.	Soluble proteïn.	Maltose.	Dextrin.	Starch.	Fat.	Pure ash.	Crude fibre.
1.	11·94	(11·67)	(1·92)	1·54	8·02	76·75	0·26	1·44	0·05
2.	17·13	(14·92)	(5·15)	0·50	11·86	63·52	2·11	2·41	2·47

There were thus gains of fat and crude fibre (0·71 and 0·98 per cent. respectively), and losses of starch (20·03), maltose (0·72), and proteïn (0·11 per cent.). No ammonia could be detected. The number given for starch in the mouldy bread was found by difference, and is slightly high, as small amounts of other substances were present. Among these, only volatile acids, oxalic acid, and mannitol could be detected, owing to the smallness of the amounts.

N. H. M.

Composition of the Ripe Husks of Capsicum. By B. v. Bittó (*Landw. Versuchs-Stat.*, **42**, 369—379).—The first analysis of capsicum seem to be that made by Buchholz (König, *Die menschl. Nahrungs- u. Genussmittel*, 2 Aufl., **1**, 148), whilst a more thorough examination of the fruit was made by Braconnot (*Ann. Chim. Phys.*, **21**, 124), who obtained capsicin, a soft, non-crystalline compound with a pungent taste, and from this capsicum-red. Witting (*Rep. Pharm.*, **13**, 366) and Tresh (*Pharm. Centr.*, **17**, 427) maintain that the active constituent is a crystalline substance termed capsaïcin. Pabst (*Arch. Pharm.*, **23**, 108) found a trace of an alkaloïd; he considers capsaïcin to be an amorphous acid; and he detected considerable amounts of free oleïc, stearic, and palmitic acids in the fruit. He concludes that the red colour of the fruit is probably carotin (compare also Felletár, *J. Pharm.*, 1868, 70; Fleischer, *Arch. exp. Path.*, **9**, 117; and Strohmer, *Chem. Centr.*, 1886, 577).

The ripe fruit examined by the author was well developed, and of a scarlet colour. The amounts of the different parts of the fruit vary considerably, owing to the varying amount of seed.

The whole fruit (1) was found to contain 90·25 per cent. of dry matter, (2) the fruit husk 85·86 per cent., (3) the seed 90·49, and (4) the placenta 87·34 per cent. The dry matter has the following composition.

	Ash.	Ether extract.	Nitrogenous matter.	Non-nitrogenous extract.	Crude fibre.	Nitrogen.
1.	6·76	10·69	19·77	39·82	22·95	3·16
2.	5·66	5·14	14·31	49·07	25·83	2·29
3.	4·35	27·95	17·22	33·07	17·36	2·93
4.	11·03	7·07	28·54	39·88	13·48	4·57

	Nitrogen as ammonia.	Nitrogen. as amides.	Proteïd nitrogen.
1.	0·217	0·093	2·321
2.	0·195	0·130	1·792
3.	0·061	0·061	2·938
4.	0·240	0·280	2·403

The following ash analyses are given of (1) the whole fruit, (2) the husks, and (3) the seed.

	K_2O.	Na_2O.	MgO.	CaO.	Al_2O_3.	Fe_2O_3.
1.	55·60	4·42	6·22	4·80	trace	1·44
2.	52·47	13·16	5·04	5·08	0·22	1·69
3.	40·12	2·50	10·43	3·46	—	0·81

	SiO_2.	Cl.	SO_3.	P_2O_5.
1.	2·04	3·88	6·44	16·82
2.	1·90	1·44	4·58	14·59
3.	1·74	2·65	4·97	33·95

As regards the manufactured products, the ordinary kinds are made by grinding the whole fruit, the stem being frequently included; they have a pale brick-red colour. The best preparations are made with the husks and seeds only. To detect adulteration, microscopic examination is necessary, as well as estimation of the ash. The pure ash is usually white or slightly greenish, and dissolves almost entirely in dilute acids. Tables are given showing the results of analyses of manufactured products. N. H. M.

Lathyrus sylvestris. By E. KINCH (*Agrl. Students' Gazette*, New Series, **6**, 108—109).—This leguminous plant has been introduced as a cultivated fodder plant suitable for poor soils, under the name of Wagner's flat pea or wood vetchling. The plot of this plant cultivated at the Royal Agricultural College, Cirencester, yielded 30 cwt. of hay per acre on May 30, 1893, and a second crop on August 4 of the same year. 1000 parts of the green stuff gave 184 parts of air-dried hay which contained 16·82 per cent. of moisture. The following analyses were made.

	Green stuff.	Dry matter of hay.
Water	84·70	—
Ash	0·86	5·62
Fibre	4·43	28·97
Ether extract	0·65	4·25
Nitrogenous matter	5·41	35·33
Soluble carbohydrates	3·95	25·83
	100·00	100·00
True proteïds	3·51	22·86

It will be seen that the nitrogen content of the hay is greater than that of peas or beans, but a much larger proportion (35 per cent.) is of an amide character. It contains twice as much nitrogen as lucerne hay, and about three times as much as meadow hay. The ether extract contained a good deal of chlorophyll. A. G. B.

Analysis of Tobacco cured by the Leaf-cure on Wire, and by the Stalk Process. By F. B. CARPENTER (*Exper. Stat. Record*, **4**, 819—821; from *N. Carolina Stat. Bull.*, No. 90A, 1893).—The two methods of curing have been already described (*Exper. Stat. Record*, **4**, 32—35). In the leaf-cure on wire, the leaves are stripped from the stalk at three different periods and strung on wires; whilst in the

stalk process the leaves are left on the stalks and kept in an ordinary barn. Owing to the manner and time of harvesting, the chemical composition of the products of the two processes varies somewhat. In the leaf-cure process, the priming of the lower leaves causes increased growth, and an increase in the percentage of proteïds and nicotine. But the loss in quality caused by this transformation is more than compensated by the gain in weight.

The results of analyses made with plants of various age showed that nitrates are almost entirely confined to the stalk and stems in the younger growth of the plant, whilst the other nitrogen compounds are more abundant in the leaves. N. H. M.

Greater Assimilability of the Nitrogen of recently formed Nitrates. By P. PICHARD (*Compt. rend.*, **117**, 125—127).—The results of all the author's experiments indicate that nitric nitrogen is most efficacious and assimilable when recently formed or when it has migrated from one base to another, especially when the new base is potash. The use of sodium nitrate as a manure in preference to the potassium salt is not only to be recommended on account of its cheapness, but also because of its conversion into the potassium salt in a soil containing potash. Again, the repeated application of small quantities of sodium nitrate has the advantage of continually furnishing the plant with newly formed potassium nitrate, besides the obvious advantage of diminished loss in drainage. It is probable that the nitrates observed by Berthelot to be formed within the plant tissues are still more assimilable than the nitrates of the soil. Vegetation will be more greatly benefited by the old methods of cultivation, which tended to induce increased nitrification in soil, than by the direct application of nitrates. N. H. M.

Combined Nitrogen in Rain. By A. PETERMANN and J. GRAFTIAN (*Bull. Stat. agron. Gembloux*, 1893, No. 52, 5—26).—Rain was collected by means of a nickeled copper collector (82 cm. in diameter), in a large glass vessel; mercuric chloride was added to prevent change. Determinations of ammonia and nitrates were made from January, 1889, to December, 1891, whenever there was sufficient water for analysis, the ammonia being determined with Nessler solution after distillation with a little potash, and the nitrates after reduction to ammonia by the zinc-copper couple. The average rainfall was 692 mm. (= 27·14 in.) per annum and contained: ammoniacal nitrogen, 1·14 per million; nitric nitrogen, 0·35 per million; total, 1·49 per million. Calculated in kilos. per hectare per annum, the amounts are as follows: nitrogen as ammonia, 7·92 kilos. (or 7·07 lbs. per acre); nitrogen as nitrates, 2·39 kilos. (or 2·13 lbs. per acre); total, 10·31 kilos. (or 9·20 lbs. per acre). This total is less than the average found at Montsouris (14·28 kilos.) and at the Italian and German stations, but higher than that obtained at Rothamsted.*

* 7·36 kilos. per hectare (= 6·57 lbs. per acre) is given as the average annual amount at Rothamsted. The authors give no indication as to where they obtained this figure, which is nearly, but not quite, the same as was obtained at Rothamsted in the years 1853–56. More recent results showed that the amounts of nitrates and

The relation of ammoniacal to nitric nitrogen is 76 : 24, which is very nearly the same as at Rothamsted (75 : 25) and at Montsouris and the German and Italian stations (73 : 27). The February rain was found to be the richest in nitrogen, that of July the poorest. The greatest rainfall was in July, the lowest in February; whilst as regards the total amounts of nitrogen in the rain, the highest was observed in August, the lowest in February. Tables are given containing the results of each of the 142 analyses made during the three years.

Separate analyses were made of hoar-frost and snow, collected in or near the grounds of the Institute. The hoar-frost contained an average amount of combined nitrogen = 7·52 per million; the snow, 7·40 per million. N. H. M.

Soluble Phosphoric acid in Superphosphate. By J. Stoklasa (*Landw. Versuchs-Stat.*, **42**, 439—457; compare Abstr., 1891, 880). —Calcium carbonate and calcium phosphate, $CaH_4(PO_4)_2,H_2O$, were well mixed in molecular proportion, treated with 500 c.c. of water, and the whole evaporated to a small bulk. It was then diluted with water, filtered, washed, and dried over sulphuric acid until the weight was constant. The residue was pure calcium phosphate, $CaHPO_4,2H_2O$. When twice the amount of calcium carbonate was employed, pure tricalcium phosphate was obtained (compare Weilandt, Abstr., 1887, 995). This reaction, showing the production of the less soluble triphosphate, is one of importance for the absorption in soil. Thus, soil, containing only 0·4 per cent. of calcium carbonate, will contain 6000 kilos. per hectare to the depth of 10 cm.; taking the maximum amount of soluble phosphate applied to the soil (100 kilos. per hectare), there will be 33 parts of calcium carbonate to 1 of monocalcium phosphate. The results of experiments with plants have shown the better effects of diphosphates as compared with the less soluble triphosphate. Chalky soils manured with monocalcium phosphate never gave as good crops (turnips, barley, and peas) as were obtained when orthophosphoric acid was employed. Inasmuch as the exact composition of superphosphates has not been ascertained, the author considers that the experiments hitherto made are incomplete and of less use than is usually supposed.

A considerable number of experiments are described in which calcium phosphate, $CaH_4(PO_4)_2,H_2O$, was submitted to the action of pure calcium carbonate in different forms, under various conditions. It was found that a mixture of the dry salts gradually changed, the amount of soluble phosphate falling from 55·4 per cent. after two hours to 21·02 per cent. after 360 days. Calcareous sandstone kept in a solution of the phosphate became covered with a layer of tricalcium phosphate. Experiments in which calcite was employed showed that more triphosphate is formed with strong than with weaker solutions.

ammonia were a good deal less than was supposed, and the total nitrogen (excluding nitrogenous organic matter) is now shown to be about 3·5 lbs. per acre per annum (compare *Jour. Roy. Agr. Soc.* [2], **17**, 241, and **19**, 313; *Trans. Chem. Soc.*, 1889, 537). N. H. M.

Zinc cylinders of different sizes were filled with sand containing 20 per cent. of pure calcium carbonate. Pure monocalcium phosphate, $CaH_4(PO_4)_2,H_2O$ (7 grams), was mixed with the top 5 cm. of the sand, and water poured on to the amount of 2 litres in 10 days. At the end of this time, each cylinder had another 2 litres of water. The drainage, which was quite clear, did not contain a trace of free phosphoric acid. Nearly the whole of the phosphates remained in the sand in an insoluble form.

In order to ascertain the effect of water on calcium phosphate, 1 kilo. of pure sand containing 19 per cent. of water was superficially treated with methyl-orange, and a gram of phosphate distributed over the surface. The pieces of phosphate immediately became red. In presence of 2 per cent. of calcium carbonate, single particles became red, the acid being neutralised. When loam was used instead of sand, the decomposition was slower. The results of these and other experiments point to the conclusion that orthophosphoric acid is first liberated and that this reacts with the calcium carbonate (2 mols.), yielding tricalcium phosphate. N. H. M.

Analytical Chemistry.

Titration of Acids by Metallic Sodium. By E. Neitzel (*Zeit. anal. Chem.*, **32**, 422—423).—The author recommends anew Hartley's proposal (this Journal, 1873, 132) to employ weighed quantities of metallic sodium for the titration of standard acids. He prefers to weigh the block of sodium under petroleum which has been heated above 100° and filtered. For this purpose a beaker containing petroleum is tared on the balance, and the block of sodium, cut clean from a larger mass as rapidly as possible, is at once slipped into the petroleum and weighed. Such a block, of about 0·7 gram, gains only about 0·17 milligram during the 15 seconds required for cutting it out. The sodium is then withdrawn with tongs, and without regarding the adhering petroleum, is treated with 75 c.c. of 88—94 per cent. alcohol in a flask fitted with a perforated cork and glass tube. When all is dissolved, water and the indicator are added, and the solution is ready for titration. M. J. S.

Estimation of Chlorine in Water. By T. Fairley (*Analyst*, **18**, 222).—The author confirms Young's statement (compare this vol., ii, 433) that water should be concentrated before titrating with silver nitrate and potassium chromate. But even then the result will not be absolutely trustworthy if the water contains traces of alkali silicate. L. de K.

Iodometric Estimation of Nitrates. By H. Gruener (*Amer. J. Sci.*, **46**, 42—50).—The author describes two new processes which, under special conditions, may be found useful.

1. *Reduction by means of Phosphoric acid and Potassium Iodide.*—A quantity of nitrate, not exceeding 0·05 gram of potassium nitrate, is introduced into a retort with 10 times its weight of potassium iodide and 17—20 c.c. of phosphoric acid (sp. gr. 1·43). The neck of the retort passes into a receiver containing a known amount of decinormal arsenious oxide, containing an excess of sodium hydrogen carbonate. For additional safety, a simple trap containing water should be attached. The solution is distilled in a current of carbonic anhydride until every trace of iodine is removed. The contents of the receiver is now titrated with iodine to find the amount of unoxidised arsenious acid. This gives the measure of the iodine evolved, and, consequently, of the nitrate present, the reaction in the retort being $2HNO_3 + 6HI = 4H_2O + 2NO + 3I_2$.

2. *Reduction by means of Antimonious Chloride.*—The dry nitrate is introduced into a diminutive retort made from a pipette shaped like a "Liebig's drier," and connected by a sliding joint, covered by india-rubber, into a Kjehldahl tube used as a receiver, and so placed that carbonic anhydride, passing through the apparatus, enters from below. The nitrate is washed down with a few drops of hydrochloric acid and a definite amount of antimonious chloride is added from a burette. The receiver is charged with 0·25 gram of potassium iodide, dissolved in recently boiled water, and is joined to a trap filled with water. After passing carbonic anhydride through the apparatus for 10 minutes, the solution is heated in an oil-bath at 103—107°, and after 15 minutes heating the receiver and trap are washed out and at once titrated with sodium thiosulphate. The solution in the retort is now diluted with solution of tartaric acid, nearly neutralised with a 25 per cent. solution of sodium hydroxide, mixed with excess of sodium hydrogen carbonate, and titrated with decinormal iodine.

The difference between the trichloride left in the retort and the iodine found in the receiver is the measure of trichloride left unoxidised by the nitrate, and the difference is the measure of the nitrate present. The test analyses are fairly satisfactory.

L. DE K.

Estimation of Nitrates by Schmitt's Method. By K. WEDEMEYER (*Arch. Pharm.*, **231**, 372—376).—10 c.c. of acetic acid, 10 grams of a mixture of equal parts of finely powdered iron and zinc, and 25 c.c. of water are placed in a flask of about 1500 c.c. capacity, a funnel is placed in the neck of the flask, and into the funnel is shaken a weighed quantity (0·3—0·8 gram) of the nitrate to be estimated, which is then washed down into the flask. Heat may be applied, so long as the temperature does not exceed 80°, and the funnel and walls of the flask must be washed down from time to time. After 10 minutes, the reduction is complete, and the ammonia may be distilled off and estimated as in Kjeldahl's method. Excellent results are obtained with nitrates; with nitrites they are too low.

C. F. B.

Methods of estimating Sulphur. By L. MARCHLEWSKI (*Zeit. anal. Chem.*, **32**, 403—411; see this vol., ii, 186).—*Gröger and Treadwell's Method.*—Pyrites is heated with metallic iron until converted into ferrous sulphide. This is decomposed by hydrochloric acid

and the liberated hydrogen sulphide absorbed in an iodine solution. With pure pyrites, the method yields excellent results, but, as a technical method, it is useless, since sulphates, such as barium and lead sulphates, would be partially reduced by the iron powder, if present, and would thus produce fictitiously high results.

Sauer's Method (this Journal, 1873, 939).—Zulkowski's simplified modification of this method is as follows. A combustion tube, 60 cm., or, for pyrites, 40 cm., long, is drawn out at one end to a long, narrow tube, which is bent downwards and connected with an absorption apparatus consisting of two bulbed U-tubes and a tube containing glass wool. The absorption liquid is 30 c.c. of an alkaline hypobromite solution, made by dissolving 180 grams of potash (free from sulphates), adding 100 grams of bromine, and making up to a litre. Next to the narrowed part of the tube comes 20—25 cm. of platinised asbestos, and at a distance of 7—10 cm. from this is placed the boat containing the substance (0·4 gram of sulphur). To the further end of the tube is attached an oxygen gas holder, with a wash bottle containing water as indicator. The tube is filled with moist oxygen while heating the platinised asbestos, and then heat is gradually applied to the substance. Finally, any sulphuric acid which may have condensed in the narrow part of the tube is driven over as far as possible by heat and then washed out. The absorption liquid is then acidified, heated, and precipitated by barium chloride. When assaying pyrites, the platinised asbestos is omitted. The method gives accurate results, but is tedious; it can, of course, be used in presence of non-volatile sulphates.

The author has been unable to get satisfactory results by Föhr's method, which consists in absorbing the hydrogen sulphide by ammoniacal zinc solution, then adding ferric sulphate, and titrating the reduced ferrous salt by permanganate. Also, in common with Friedheim (Abstr., 1886, 739), he considers Klobukow's method (Abstr., 1885, 1159) as useless. M. J. S.

Treatment of Barium Sulphate in Analysis. By J. I. Phinney (*Amer. J. Sci.*, **45**, 468—472).—The author, having carried out a large number of experiments, concludes that the barium sulphate should preferably be collected on a Gooch's asbestos filter, so as to avoid reduction of the sulphate by the filter-paper. Alkali chlorides contaminate barium sulphate thrown down in the presence of an excess of sulphuric acid, and are not completely removed by ignition and subsequent treatment with hydrochloric acid. According to the author, the only good method for purification is either to fuse, according to Fresenius, with sodium carbonate, extract, and reprecipitate as sulphate, or to evaporate from solution in strong sulphuric acid as proposed by Mar. L. de K.

Influence of Nitric acid and Nitro-hydrochloric acid on the Precipitation of Barium Sulphate. By P. E. Browning (*Amer. J. Sci.*, **45**, 399—404).—The author has proved by a series of carefully made experiments that the presence of an excess of nitric acid, or nitro-hydrochloric acid, amounting to 10 per cent. by volume of

the liquid, is not only not to be avoided in estimating barium as sulphate, but it is actually to be recommended. When precipitated from such acid solutions, the sulphate is coarsely crystalline and heavy, and less liable to carry down impurities; and even in certain special cases where there are substances which exercise a solvent action, the precipitation is made complete.

To make sure that the correctness of the results was not due to a compromise between any loss caused by the solvent action of the acids and the increase caused by the co-precipitation of alkali salts, &c., the author took the precaution of recrystallising the barium sulphate from hot concentrated sulphuric acid. It was then again washed with water. L. DE K.

Emmerton's Process for the Estimation of Phosphorus. By H. C. BABBITT (*Chem. Centr.*, 1893, i, 957—958; from *J. anal. Chem.*, **7**, 165—168).—If the precipitation with ammonium molybdate is conducted at a temperature exceeding 25°, the precipitate may contain arsenic. The yellow precipitate contains 1·63 per cent. of phosphorus. The precipitation is complete within five minutes if a whirling apparatus is used. The reduction by means of zinc and sulphuric acid gives the compound $Mo_{12}O_{19}$; reduction by means of zinc-dust is not to be recommended, as constant results cannot be obtained. L. DE K.

Colorimetric Analysis of Phosphorites. By A. NASTIUKOFF (*J. Russ. Chem. Soc.*, **25**, 31—42).—The author has made a number of experiments on natural and artificial phosphorites, which tend to show the possibility of estimating the amount of phosphoric acid present in them by means of the bluish-grey colour produced when they are heated with insufficient access of air. A platinum crucible is two-thirds filled with finely-sifted phosphorite, and heated with the lid on in a gas flame for 10 to 15 minutes, during which time the lid is twice or thrice removed, and the contents stirred up with a platinum wire. No details are given as to how the colorimetry is carried out. The method is said only to hold within certain limits of composition, and not for all phosphorites. J. W.

Estimation of Phosphorus in Steel. By C. B. DUDLEY and F. N. PEASE (*Chem. Centr.*, 1893, i, 957; from *J. anal. Chem.*, **7**, 108—115).—1 gram of the sample is dissolved, in an Erlenmeyer flask, in 75 c.c. of nitric acid of sp. gr. 1·15; when dissolved, it is boiled for a minute and mixed with 10 c.c. of a solution of potassium permanganate, and then again boiled until manganese dioxide begins to separate. The liquid is now cleared by the cautious addition of pure ferrous sulphate, heated to 85°, and mixed with 75 c.c. of ammonium molybdate solution at 27°. After shaking for five minutes in the authors' apparatus, the precipitate is washed with solution of ammonium sulphate until the washings give no coloration with ammonium sulphide, and then dissolved in a mixture of 5 c.c. of ammonia and 25 c.c. of water. The solution is now mixed with 10 c.c. of strong sulphuric acid, diluted to 200 c.c., and filtered through a tube containing a perforated platinum crucible filled with granulated zinc. The lower end of the tube

is fitted with another perforated platinum crucible containing sand. The filtrate is now titrated with potassium permanganate. The amount of permanganate which represents 1 gram of iron equals 0·0172444 gram of phosphorus. L. DE K.

Estimation of Phosphorus in Iron in presence of Arsenic. By E. D. CAMPBELL (*Chem. Centr.*, 1893, i, 795; from *J. Anal. Chem.*, **7**, 2—3).—The author estimated the phosphorus gravimetrically as ammonium phosphomolybdate. In some experiments, potassium arsenate was purposely added in order to see whether the presence of arsenic would interfere with the process. The results showed conclusively that, unless the arsenic is first removed by means of oxalic acid, serious errors will arise. L. DE K.

Estimation of Potassium. By A. VILLIERS and F. BORG (*Compt. rend.*, **116**, 1524—1527).—See this vol., ii, 521.

Quantitative Separation of Cæsium. By H. L. WELLS (*Zeit. anorg. Chem.*, **4**, 341—345; and *Amer. J. Sci.*, **46**, 186).—See this vol., ii, 521.

A Reaction of Cupric Salts. By E. LENOBLE (*Bull. Soc. Chim.* [3], **9**, 137—138).—On the addition of potassium mercuric iodide to cupric sulphate in aqueous solution, a bright red precipitate is formed, and can be freed from iodine by treatment with water. The compound appears to be *cuprous mercuric iodide*, $Cu_2I_2,2HgI_2$; but its exact composition is probably dependent on that of the potassium mercuric iodide and on the concentration of the reagents. As a qualitative test, the reaction serves to indicate the presence of copper in solutions containing 1 part in 1000. J. B. T.

Volumetric Estimation of Arsenic and Antimony. By S. GYÖRY (*Zeit. anal. Chem.*, **32**, 415—421).—Arsenious and antimonious oxides are converted into the respective pentoxides with quantitative accuracy by the action of potassium bromate, the quantities concerned agreeing with the equation $2KBrO_3 + 2HCl + 3As_2O_3 = 2KCl + 2HBr + 3As_2O_5$. The method has so far been tested only on pure sodium arsenite (Fowler's solution) and potassium antimonyl tartrate. A decinormal bromate solution is obtained by drying the salt at 110° and dissolving 2·7850 grams to 1 litre. The arsenious or antimonious solution is freely acidified with 10 per cent. hydrochloric acid, a drop of a 1 per cent. solution of methyl-orange is added, and the bromate solution is run in until the methyl-orange pink colour disappears, leaving the liquid colourless. The end reaction is extremely sharp, one-tenth of a drop of bromate sufficing to discharge the colour. M. J. S.

Estimation of Chromium in Products of the Iron Industry. By G. GIORGIS (*Gazzetta*, **23**, i, 277—284).—The author has devised the following rapid and accurate method of estimating chromium in steel or other metallurgical products. The steel is dissolved in sulphuric and nitric acids, and the solution made up to 1 litre.

250 c.c. of this is then rendered just alkaline with soda, and potassium permanganate is added to the heated solution until a permanent red colour is produced; after cooling, the excess of permanganate is destroyed by hydrogen peroxide, and the solution made up to 500 c.c.; 400 c.c. of this is then taken off by filtration, acidified with sulphuric acid, reduced with sulphurous anhydride, and evaporated to 200 or 100 c.c. This solution is then titrated against a standard solution containing 6 grams of potassium permanganate, 40 grams of potassium carbonate, and 0·5 gram of caustic potash per litre. The chromium solution is run into the boiling permanganate until the red colour gives place to the golden yellow of potassium chromate. Test analyses are given. W. J. P.

Colorimetric Estimation of Small Quantities of Uranium in Minerals. By A. Bruttini (*Gazzetta*, **23**, i, 251—257).—In order to separate the uranium from minerals containing it, the author treats the powdered substance with nitric acid, and eliminates the silica by evaporation to dryness and heating the residue; this is then taken up by dilute nitric acid. On adding ammonium hydrogen sulphide and ammonium carbonate to the filtered solution and heating, the uranium and arsenic and part of the antimony, tin, copper, and nickel remain dissolved, whilst all the other heavy metals are precipitated. The filtered solution is acidified with nitric acid, and, after filtration, can only contain uranium, copper, and nickel; if the last two metals are present, the uranium is precipitated with ammonia, collected, and dissolved in boiling dilute nitric acid. The uranium solution is then evaporated, the ammonium salts driven off by heat, the residue dissolved in dilute nitric acid, and the solution made up to a known volume; aliquot parts are then taken for the colorimetric determination. This is performed by means of the author's colorimeter, the depth of colour produced by mixing potassium ferrocyanide with a standard solution of uranium being compared with that obtained with the solution to be tested. W. J. P.

Estimation of Sugar in Tomatoes. By G. C. Caldwell (*Exper. Stat. Record*, **4**, 802; from *N.Y. Cornell Stat. Bul.*, No. 49, 1882).—The fruit is dried at 100°, extracted with 90 per cent. alcohol in a continuous extracting apparatus, and the sugar determined in the extract by the gravimetric copper method. Neither the polariscope nor the Fehling test are trustworthy for direct estimation in tomatoes, on account of the possible action of organic acids and the presence of other reducing substances besides sugar.

The acidity was determined by means of standard aqueous potash, and calculated as malic acid. N. H. M.

Detection and Estimation of Glucose by means of Phenylhydrazine. By E. Laves (*Arch. Pharm.*, **231**, 366—372).—To detect sugar in urine, 10 c.c. of it is mixed with 20 drops of phenylhydrazine and 3 grams of acetic acid, and boiled; yellow glucosazone is precipitated. To detect traces of glucose, albumin, &c., must first be pre-

cipitated with lead acetate, and the filtered solution concentrated and treated as above.

This reaction may advantageously be used to estimate glucose when the latter is present in small quantity. The solution, which should contain about 0·2 per cent. of glucose, is treated with a large excess of phenylhydrazine and acetic acid, in amounts respectively 20 and 30 times that of the glucose present, and boiled for $1\frac{1}{2}$ hours; the precipitate of osazone is collected, dried, and weighed, and a correction is applied for that left in solution. The results vary very much as the relative amounts of phenylhydrazine present alter, but the author states that the method is not inferior to that of Fehling, or to the polarimetric one, for estimating small quantities of sugar.

C. F. B.

Gravimetric Estimation of Furfuralhydrazone. By W. H. Krug (*Chem. Centr.*, 1893, i, 861; from *J. Anal. Chem.*, **7**, 68—77).—Pentoses are now often estimated by converting them into furfuraldehyde by distillation with hydrochloric acid. The furfuraldehyde is then converted into the hydrazone by the addition of phenylhydrazine acetate; the precipitate should be allowed to settle for a few hours before collecting. As it adheres obstinately to the sides of the beaker, the author advises that it should be redissolved in alcohol and the solution evaporated in a tared dish. The residue is then completely dried at 60° in a current of air, and weighed. L. de K.

Volumetric Estimation of Acetone. By F. Robineau and G. Rollin (*Chem. Centr.*, 1893, i, 961—962; from *Mon. Sci.* [4], **7**, 272—274).—The process consists in converting the acetone into iodoform, by dissolving it in aqueous soda containing potassium iodide and adding a standard solution of sodium hypochlorite until a drop of the solution gives a blue spot on starch paper.

To standardise the hypochlorite solution, 2 grams of pure acetone is made up to 500 c.c. 100 c.c. of this solution is mixed with 10 grams of potassium iodide and 20 c.c. of aqueous soda (sp. gr. 1·24). The hypochlorite is then run in until only a faint turbidity is produced, when the starch test should be applied. Methyl or ethyl alcohol do not interfere with the process, and paraldehyde only when present in large quantity. L. de K.

Detection and Estimation of Thiocyanates in Ammonium Sulphate. By H. Offermann (*Bied. Centr.*, **22**, 507).—The ammonium sulphate obtained in coal gas purification, and used as manure, contains, according to the manner in which it is produced, more or less thiocyanate, which is injurious to vegetation. In order to detect this, the salt is extracted with absolute alcohol and the extract tested with ferric chloride solution. In estimating the amount of thiocyanate, an alcoholic solution is prepared by extracting the salt (5 grams) for an hour with methyl or ethyl alcohol. The analysis may be continued by any of the following methods: (1) colorimetrically, by comparing with an iron thiocyanate solution of known strength; (2) gravimetrically, by means of silver solution; (3) estimation of the nitrogen by Kjeldahl's method; (4)

oxidation of the residue with bromine and estimating the sulphuric acid. N. H. M.

Estimation of Succinic acid. By A. RAU (*Zeit. anal. Chem.*, **32**, 482—486; from *Arch. f. Hygiene*, **14**, 225).—The following method was devised in the course of an investigation into the influence of varying conditions of fermentation on the formation of succinic acid. 100 c.c. of the wine is evaporated to a syrup, extracted repeatedly with boiling alcohol, and the cooled alcoholic solutions filtered, mixed, and distilled. The residue is dissolved in a little hot water, and the cooled solution filtered, if turbid; it is then treated with barium nitrate, 3—4 vols. of 90 per cent. alcohol are added, and the mixture is well stirred. The precipitate, containing tartaric, malic, and succinic acids, is collected, washed well with 70 per cent. alcohol, warmed with sodium carbonate solution, and filtered; the filtrate is neutralised with nitric acid, evaporated to a small bulk, and, after neutralisation with ammonia, is precipitated with a magnesia mixture, made with magnesium nitrate, ammonium nitrate, and ammonia. The precipitate, which contains the tartaric acid, is filtered off after three or four hours' repose; the filtrate is heated with potash until all the ammonia is expelled, then filtered from magnesia, neutralised exactly with nitric acid, diluted to 100—150 c.c., and precipitated with silver nitrate (1 : 20). Silver nitrate precipitates succinic acid completely, but produces precipitates in malic acid solutions only when they are stronger than 1 : 800. The precipitate is collected on a tared filter, washed well, dried, and weighed. As a control, it may be ignited and the silver weighed. Should the solution, to which silver nitrate is to be added, contain chlorides, which may happen if too much alcohol has been added after the barium nitrate, or too long an interval has been allowed before filtration, a portion of it must be evaporated, incinerated, the chlorine determined, and a corresponding quantity of silver chloride subtracted from the weight of the silver succinate. Proof estimations gave 102, 98·7, and 103 per cent. when working with 0·1 gram in 100 c.c.

The fermentation experiments show that a low temperature does not diminish the production of succinic acid; that the absence or presence of air is without influence; that the addition of nutrient substances does not favour its formation; but that an increased production is induced by a vigorous action of the yeast cells.

M. J. S.

Examination of Tartaric and Citric acids for Lead. By M. BUCKET (*Zeit. anal. Chem.*, **32**, 465; from *Répert. Pharm.*, **48**, 246).—200 grams of the substance is dissolved in 600 c.c. of water, and made feebly alkaline with ammonia. Any insoluble matter is collected, washed, dissolved in nitric acid, and the lead precipitated by sulphuric acid and alcohol. The lead thus found was originally present in the metallic state. The ammoniacal solution is now acidified with hydrochloric acid, and precipitated with hydrogen sulphide solution. The lead sulphide is converted into the sulphate in the same way as above; its amount gives the lead originally present as lead compounds. M. J. S.

Calcium Tartrate from Distillery Residues; its Estimation and Purification. By C. ORDONNEAU (*Bull. Soc. Chim.* [3], **9**, 66—70).—The process adopted in order to obtain calcium tartrate from the vinasse is to saturate the latter with lime; if, however, it contains other acids, such as malic, in addition to tartaric, then lime is added in amount insufficient for complete neutralisation; in this case, the calcium tartrate precipitated is fairly pure, whereas, had the solution been neutral, instead of still acid, much malate would also have been precipitated.

To estimate tartaric acid in a mixture of calcium tartrate and malate, 20 grams of the powdered substance is dissolved in 20 c.c. of hydrochloric acid and 80 c.c. of water, and the whole made up to 202 grams if the original substance contains more than 75 per cent. of tartrate, to 203 grams if it contains less. 50 c.c. of the solution is taken, 2 c.c. of a 25 per cent. solution of citric acid (to dissolve aluminium phosphate) and 10 c.c. of 25 per cent. calcium acetate added, and the mixture shaken violently. After a precipitate has formed, 5 c.c. more acetate is added, the mixture shaken, allowed to settle for half an hour, collected, and washed. The precipitate is dried on the filter on a copper plate over a water-bath, transferred as completely as possible to a nickel capsule, and heated on the water-bath with constant stirring until the moment when the clots of moist tartrate break up into a fine powder; the salt then contains $4H_2O$. Its weight multiplied by 20 gives the percentage of calcium tartrate in the substance examined, after adding 2 per cent. to allow for what is left on the filter paper and dissolved in the calcium chloride. Or 50 c.c. of the solution is taken as before, heated to boiling in a porcelain capsule, neutralised with clear lime-water, using phenolphthaleïn as indicator, 2 c.c. of 25 per cent. citric acid solution added, and the precipitate collected, washed, dried, and weighed as before, adding this time 4 per cent. to the result, as calcium tartrate is more soluble in a hot solution of calcium chloride. C. F. B.

Estimation of Uric acid. Behaviour of Uric acid in Solution. By I. KREIDL (*Monatsh.*, **14**, 109—115).—To the solution of uric acid, a moderate excess of (normal) potash solution is added, and then a considerable excess of N/30 iodine solution; after standing for three-quarters of an hour, the solution is acidified with hydrochloric acid. The excess of iodine then separates, and is titrated with N/30 thiosulphate, starch being used as an indicator; 3·5 atoms of iodine correspond with 1 mol. of uric acid under these circumstances, and 2·3 if the hydrochloric acid is added immediately after the iodine solution. A solution of uric acid, and still more one of potassium urate, when allowed to remain in contact with air, gradually loses its power of reducing iodine solution, but this is due to the presence of microbes, for a sterilised aqueous solution of uric acid does not undergo this change in a sterilised atmosphere; potassium urate does, however, if the solution is boiled, or if a slight excess of potash is present. C. F. B.

Estimation of Solids and Fat in Milk. By J. B. KINNEAR (*Chem. News*, **68**, 1—2).—The following process may be used either for cream or for rich or skimmed milk. About 1 gram of milk is poured on to a thin, flat tared glass plate, about 2½ inches in diameter, and after weighing is dried in a hot air chamber, being loosened from the glass by a steel scraper before it is quite dry. The dry solids are weighed and transferred to a ½-oz. tared stoppered bottle, 3 to 4 c.c. of ether is then added, the stopper tied down, and the bottle immersed in warm water for a few minutes, shaken for one minute, then cooled and weighed. As much of the clear solution as possible is now poured into a tared watch glass, the stopper immediately replaced, and the bottle again weighed. The fat on the watch glass is also weighed, and from the data obtained, the fat remaining in the bottle, the total fat in the ether and in the milk are calculated. The error arising from the evaporation of the ether during the pouring out into the watch glass is in the author's opinion a negligible quantity for practical purposes, and almost disappears if light petroleum is used as the solvent. D. A. L.

The Elaïdin Reaction. By A. LIDOFF (*J. Russ. Chem. Soc.*, **24**, 515—524).—Oils which do not dry become solid when treated with nitrous acid, on account of the conversion of the oleïn they contain into elaïdin. Drying oils, on the other hand, remain liquid under similar treatment, although at the same time their chemical and physical properties are considerably modified. Their sp. gr. increases as well as their viscosity and saponification ratio. The iodine coefficient and Hehner's ratio diminish. All oils after treatment with nitrous acid contain nitrogen, varying in amount from 1 to 2·5 per cent. These substances may be reduced by various agents, yielding new substances which probably contain the amido-group. The free unsaturated acids yield no such compounds. J. W.

Estimation of Caffeïne. By A. GRANDVAL and H. LAJOUX (*J. Pharm.* [5], **27**, 545—549).—The finely powdered material (5 grams) is stirred with a well shaken mixture of ether (5 grams) and officinal (French) solution of ammonia (1 gram) in a porcelain capsule; the powder is then completely extracted with chloroform (50 c.c.) in a reflux extraction apparatus, the chloroform is driven off from the extract, and the residue, after being moistened with 10 per cent. sulphuric acid (1 c.c.), is extracted several times, to complete exhaustion, with small quantities of hot water, and the aqueous solution is filtered, the funnel being covered with a watch-glass. In the case of roasted coffee, the aqueous solution is made alkaline with soda, and completely extracted with chloroform, the chloroform extract is evaporated, and the residue of caffeïne is weighed. In other cases, the solution is treated with excess of ammonia, evaporated, the residue completely extracted with chloroform, the chloroform extract filtered and evaporated, and the residue of caffeïne weighed. The process is accurate, and takes only three hours to perform. Black tea contains 2·9, raw coffee 0·988, roasted coffee 0·9, and kola nut 2·3 per cent. of caffeïne. C. F. B.

Estimation of Emetine in Ipecacuanha Root. By C. KELLER (*J. Pharm.* [5], **27**, 465—467; from *Pharm. Post*, **25**, 913; compare this vol., ii, 398).—The methods of Flückiger, Kremel, and Lloyd were tried and found defective; the following is recommended:—Powdered ipecacuanha (15 grams) is placed in a flask with alcohol of 90° (148 c.c.) and some hydrochloric acid (2 c.c.; sp. gr. = 1·12), the flask is corked, and the mixture digested for four days at 40°, being frequently shaken. When cold, 100 c.c. of the clear liquid is withdrawn, mixed with 20 c.c. of a solution of neutral lead acetate (1 gram) in 50 per cent. alcohol (10 grams) and 1·5 grams of slaked lime, and evaporated on the water bath to a thin paste; it is then mixed with 5 grams of powdered glass, and evaporated to dryness, with frequent stirring. The dry mass, after being powdered, is extracted with chloroform, the chloroform is driven off from the extract, and the residue weighed. It is then treated with 2 c.c. of normal hydrochloric acid, and washed with water; the residual resin is weighed, and its weight subtracted from that of the first residue; the difference is the weight of the emetine, which was dissolved out by the hydrochloric acid. Various specimens of ipecacuanha examined contained from 1·81 to 2·37 per cent. of emetine.

C. F. B.

Analysis of Ethereal Oils. By R. BENEDIKT and H. STRACHE (*Monatsh.*, **14**, 270—277).—As an aid in the identification of ethereal oils, the authors have determined the "carbonyl number" ("Carbonylzahl") for many of these, that is, the amount of carbonyl oxygen in 1000 parts of the oil. The value of this coefficient varies from 0·9 in the case of oil of cedar wood to 145·3 in the case of oil of bitter almonds; it has been determined for a number of different oils and their commercial varieties, but the table of results is too long to reproduce. The method adopted is to boil a weighed quantity of the oil with phenylhydrazine hydrochloride (the relative amounts varying as the oil contains more or less carbonyl oxygen) and sodium acetate in amount equal to 1½ times that of the hydrochloride for a quarter of an hour in alcoholic solution. The whole is then made up to 100 c.c., the hydrazone and unattacked oil filtered off through a dry folded filter, and the excess of phenylhydrazine determined by oxidising 50 c.c. of the filtrate with hot Fehling's solution, and measuring the nitrogen evolved (Abstr., 1892, 1322). An improved method of measuring the nitrogen is described.

C. F. B.

Hüfner's Method of estimating Urea. By W. CAMERER (*Zeit. Biol.*, **29**, 239—246).—It is urged that this method of estimating urea is of sufficient accuracy for all purposes. There are certain points of detail to be attended to which are pointed out. Among the facts noted may be mentioned the following. The alkaline solution need not be absolutely fresh for every estimation; keeping for 24 hours makes only a very small difference in the result. The yield of nitrogen from urine is slightly greater when sugar is added, but not sufficient to account for the increase of urea found in diabetes.

W. D. H.

General and Physical Chemistry.

Absorption of Light by Liquid Bromine. By C. Camichel (*Compt. rend.*, **117**, 307—309).—Liquid bromine, even in layers not greatly exceeding in thickness a wave-length of the line D, has a very energetic absorbing action. Measurements made with a Gouy spectrophotometer on very thin layers of bromine enclosed between glass plates such as serve for the production of Newton's rings, show that when the abscissæ are the thicknesses of the layer of bromine, and the ordinates are the values of log I_2/I_1, the results are represented by right lines. The absorption of thin layers of bromine, therefore, follows the exponential law. The coefficients of absorption are, for λ 589 (Na), $0{\cdot}517 \times 10^3$; for λ 569, $0{\cdot}981 \times 10^3$; and for λ 535 (Tl), $2{\cdot}49 \times 10^3$. C. H. B.

Product of Asymmetry. By P. A. Guye (*Compt. rend.*, **116**, 1378—1379).—The product of asymmetry is defined as the product of the six perpendiculars drawn from the centre of gravity of a tetrahedron to the six planes of symmetry. If the masses of the four groups united to a carbon atom are either placed at the four angles of the regular tetrahedron, or at variable distances from these, or are laterally displaced, the above product will be represented in each case by a formula of a more or less complex nature. The author deduces general expressions for the product in the cases named, but, as each of these contains a number of unknowns, it is impossible to put them to a strict experimental verification. Some general applications will, however, be given later. H. C.

Rotatory Power of a Substance belonging to an Homologous Series. By P. A. Guye (*Compt. rend.*, **116**, 1451—1454).—The author considers, with the aid of the formulæ for the product of asymmetry deduced in former papers (this vol., ii, 204, and preceding abstract), the effect on the rotatory power of a substance *Cabcd* that will be produced by a gradual and regular increase in the mass of *a*. If the asymmetry of the molecule is not very pronounced, a gradual increase in *a* may have the effect of increasing the rotatory power until a maximum is reached, from which a decrease will take place. If the asymmetry is of a very pronounced character, the change in the rotatory power may be of various kinds, but it is not possible to give general rules for these cases. H. C.

Rotatory Power of Ethereal Salts of Valeric and Glyceric acids. By P. A. Guye and L. Chavanne (*Compt. rend.*, **116**, 1454—1457).—In order to submit certain deductions, made by one of the authors with regard to the rotatory powers of substances belonging to an homologous series (preceding abstract), to the test of experiment, the rotatory powers of certain ethereal salts of valeric acid have been measured. Among the alkyl salts, the methyl compound

is found to have the greatest rotation, greater than that of the acid itself, a maximum in rotatory power therefore existing in this place, as predicted by theory. The rotatory powers of ethereal salts of glyceric acid, measured by Frankland and MacGregor (Trans., 1893, 511), also rise to a maximum in the case of the alkyl salts, this occurring, in this instance, with the propyl compound. H. C.

Influence of Organic Solvents on Rotatory Power. By Freundler (*Bull. Soc. Chim.*, [3], **9**, 409—413).—The rotatory power of ethereal salts of the type COOR·CHO(R'CO)·CHO(R'CO)·COOR is compared with the corresponding quantity deduced from observations on their solutions in dry acetone, absolute alcohol, 94 per cent. alcohol, benzene, chloroform, and carbon tetrachloride respectively. Measurements were made at temperatures kept nearly constant, the extreme limits being 20° and 28°.

Dry acetone, absolute alcohol, and 94 per cent. alcohol have very little effect on the rotatory power at concentrations of about 1 gram in 20 c.c. of the solvent.

Benzene, chloroform, and carbon tetrachloride lower the algebraic value of the rotatory power to a considerable extent, differing with the solvent used. Probably molecular compounds are formed between these solvents and the ethereal salts, a view upheld by the fact that increase of temperature increases algebraically the rotatory power, bringing this quantity nearer to its normal value as the conditions become more favourable to the dissociation of molecular combinations. The temperature effect is marked with chloroform solutions.

In acetone solutions, the rotatory power decreases slowly as the concentration increases; in chloroform solutions, the reverse is the case beyond a certain concentration. If the formation of molecular combinations be admitted, this fact is readily explained by the increasing difficulty of forming the compound, as less of the solvent remains free. W. T.

A One-Volt Standard Cell. By H. S. Carhart (*Amer. J. Sci.*, [3], **46**, 60—66).—The author employs a one-volt standard cell, of the same form as the Clark standard. The tube contains pure mercury in contact with a platinum wire; on this is placed mercurous chloride paste, covered with zinc chloride solution. A cork diaphragm, with asbestos packing under it, is employed to keep the paste in position, and above it is placed more zinc chloride solution containing an amalgamated zinc rod; the whole is then hermetically sealed. The sp. gr. of the zinc chloride solution necessary to give an E.M.F. of 1 volt at 13·7° is 1·391 at 15°. The internal resistance of the cell is about 1500 ohms, and it seems to suffer no permanent change by heating at 50°. It is noteworthy that this cell has a positive and very small temperature coefficient; from 10° to 40° the temperature curve is approximately a straight line, and the E.M.F. is obtained from the equation $E_t = 1 + 0{\cdot}000094(t - 15)$. Above 40°, the curve rises and involves the third power of $t - 15$. The E.M.F. is observed to lag somewhat as the temperature falls; the hysteresis is, however, very slight, being equivalent to about 3° difference of temperature.

The sign of the temperature coefficient of standard cells depends on the relative magnitudes and signs of the thermo-E.M.F.'s at the two sides of the couple. These may be experimentally determined by means of an H-tube containing the solution and electrodes of the metal concerned; one limb of the tube is kept in melting ice, and the other in a bath at the required temperature. The E.M.F. set up is determined electrostatically, and is balanced against a standard E.M.F. Employing this method, the author has measured the thermo-E.M.F. of the voltaic series Cu | $CuSO_4$ | Cu between 0° and 50° as +0·00073 volt, and has hence calculated the values for several other series, and compared them with the experimental values. The data given by Bouty, and by Chroustchoff and Sitnikoff (*Compt. rend.*, **108**, 937), would show the temperature coefficient of the author's cell to be small but negative. Bouty's thermo-E.M.F. for the series Zn | $ZnCl_2$ | Zn is, however, too large; the author finds it to be 0·000584, a number from which the temperature coefficient of the new cell is calculated as practically identical with the value obtained experimentally.

W. J. P.

Electrical Conductivity of Flames and Gases. By A. de Hemptinne (*Zeit. physikal. Chem.*, **12**, 244—274).—Two platinum electrodes were so connected, one with a galvanic element and the other with a capillary electrometer, that the presence of a conducting substance between them was indicated by the mercury in the electrometer assuming a negative charge and moving upwards in the capillary. No effect was noticed when the electrodes were immersed in nitric oxide and oxygen gases in the act of combining, even when the electromotive force employed was 100 volts. The same negative result was obtained when the reacting pairs of gases were hydrogen bromide and chlorine, and hydrogen chloride and ammonia.

The influence of temperature was noted by placing the electrodes at the same relative part of a bunsen flame, the combustible gas containing variable quantities of an indifferent gas. The hydrogen flame and the carbonic oxide flame conduct well, the conductivity increasing with rise of temperature.

Observations were also made on the conductivity of explosive mixtures at the moment of explosion. There is decided conductivity in the case of oxygen-hydrogen and chlorine-hydrogen explosions, and a much slighter amount in the case of oxygen-carbonic oxide.

Although hydrogen chloride and ammonia show no conductivity by themselves at moderate temperatures, dissociating ammonium chloride conducts fairly well. Ammonium bromide behaves similarly, but vapour of amylene bromide (although it is dissociated) does not conduct. Nitric oxide is a non-conductor.

J. W.

Experiments with the Manocryometer. By L. E. O. de Visser (*Rec. Trav. Chim.*, **12**, 101—140).—The "manocryometer" employed by the author is a stout glass vessel, resembling Ostwald's modification of the Sprengel density tube. The short capillary is sealed off, and the long capillary has two small bulbs on the ascending portion, the horizontal part being very long and sealed at the end. The purpose of the apparatus is to determine the melting point of a sub-

stance under pressure. The principal bulb (46 c.c.) is filled with the experimental substance, the lower part of the capillary and the lower bulb with mercury, the upper bulb (1·3 c.c.) and the rest of the capillary (0·13 c.c.) being filled with air, which acts as a manometer. The substance is heated to a temperature (constant within 0·001°) a little above its melting point for half an hour, and the pressure is then read off. This gives the value $\frac{dT}{dp}$ in James Thomson's formula $\frac{dT}{dp} = 10333 \cdot \frac{T}{E} \cdot \frac{\sigma - \tau}{r}$. The author determined $\frac{dT}{dp}$, T, σ, $\sigma - \tau$, and r for acetic acid, as well as the value $\frac{\sigma - \tau}{r}$, directly by the use of an acetic acid calorimeter analogous to Bunsen's ice-calorimeter. His results are as follows.

Melting point of acetic acid (T) at 760 mm. = 16·6713° (mercury thermometer), or 16·5965° (hydrogen thermometer).

Sp. gr. of liquid at melting point = 1·05315 compared with water at 4°, whence sp. vol. (σ) = 0·94953.

Change of volume on fusion of 1 kilo. in cubic metres ($\sigma - \tau$) = 0·00015955, whence sp. vol. of solid (τ) at melting point = 0·78998, or sp. gr. of solid at the melting point = 1·26585.

Heat of fusion (r) at melting point = 46·416 Cal.

$\frac{\sigma - \tau}{r}$ calculated = 0·0000034374.

$\frac{\sigma - \tau}{r}$ found directly = 0·0000034425.

$\frac{dT}{dp}$ calculated from Thomson's formula = 0·02421°.

$\frac{dT}{dp}$ observed with manocryometer = 0·02435°.

J. W.

The Speed of Vaporisation of Compounds in Different Atmospheres. By R. D. Phookan (*Zeit. anorg. Chem.*, **5**, 69—74).—The author has already shown that the time of vaporisation of a compound in atmospheres of vapours of different densities is constant (*Zeit. anorg. Chem.*, **2**). In this paper he points out some sources of error in his earlier experiments, and figures an improved apparatus. From the table comprising his results, it appears that the quantity of normal propyl alcohol used in the experiments varied from 0·0264 to 0·0268 gram; that the volume of vapour measured varied from 13·7 to 15·0 c.c., and that the time of vaporisation in vapour of methyl alcohol, ether, chloroform, perchloromethane, and in hydrogen varied from 12 to 14 seconds, whilst the same value in air was 23 seconds, and in carbonic anhydride 26—27 seconds. A. G. B.

Diffusibility of certain Gases through a Caoutchouc Membrane. By A. Reychler (*Bull. Soc. Chim.*, [3], **9**, 404—409).—Sulphurous anhydride combines with caoutchouc just as it combines

with camphor. In an atmosphere of sulphurous anhydride, caoutchouc absorbs the gas with consequent reduction of pressure; under reduced pressure, or in the air, the absorbed gas is given off, increasing the partial pressure due to the sulphurous anhydride. Hence the explanation of the apparently abnormal diffusion of sulphurous anhydride and carbonic anhydride through membranes of caoutchouc. When a tube, closed at one end with a thin caoutchouc membrane, is inverted over mercury and filled with sulphurous anhydride, or a mixture of sulphurous anhydride and carbonic anhydride, the mercury rises in the tube, as observed by Pictet, not because of any abnormal diffusibility of these gases through caoutchouc, but because a compound is formed with the caoutchouc reducing the pressure within the tube and almost simultaneously the gas absorbed is given off from the upper surface of the membrane by the decomposition of this compound in the free air. The true diffusion of atmospheric gases through the septum in the opposite direction is so comparatively slow that the pressure in the tube is brought almost to zero.

With thicker membranes, the penetration of the gas to the outer surface is greatly hindered, and hence the rate of apparent diffusion is lowered. Carbonic anhydride traverses caoutchouc at a much slower rate than sulphurous anhydride. W. T.

Diffusion in Aqueous Solutions of Mixed Salts. By L. Liebermann and S. Bugarszky (*Zeit. physikal. Chem.*, **12**, 188—195).—Suppose a solution, A, containing 1 gram-molecule of sodium chloride and 1 gram-molecule of potassium nitrate per litre is brought into diffusion-contact with a solution, B, containing 1 gram-molecule per litre of sodium chloride; then, if double decomposition takes place in the first solution with consequent formation of some potassium chloride and sodium nitrate, sodium chloride will diffuse from B to A, and potassium chloride from A to B. Since the rates of diffusion of these salts are different, the amount of chlorine in different parts of the solution should vary. If, however, Arrhenius' theory is correct, and all the salts are dissociated into ions, no double decomposition can take place and the amount of chlorine in different parts of the solution will remain the same, although the relative amounts of potassium and sodium go on varying.

The authors have conducted experiments of this nature, and find that there is no appreciable variation in the amount of chlorine in the different parts of the solution. J. W.

Dissociation Ratio of Salts. By A. A. Noyes (*Zeit. physikal. Chem.*, **12**, 162—166; compare Abstr., 1892, 1143).—While admitting the applicability of the method proposed by Arrhenius for deciding between the respective values of the electrolytic conductivity and the influence on solubility for determining the dissociation ratio of salts in aqueous solution, the author denies the validity of Arrhenius's conclusions (this vol., ii, 364). J. W.

Freezing Point of Solutions of Sodium Chloride. By S. U. Pickering (*Ber.*, **26**, 1977—1979).—A rejoinder to Jones (this vol., ii, 447).

Nature of certain Solutions and a new means of investigating them. By M. C. Lea (*Amer. J. Sci.*, [3], **45**, 478—487).—"Herapathite" (the double sulphate and hydriodide of quinine tetriodide) is converted by digestion with barium carbonate in alcoholic suspension into a substance which contains no sulphuric acid and is soluble in alcohol, and this substance is reconverted by the smallest trace of free sulphuric acid into an equivalent amount of herapathite.

In applying the test, the finely-powdered crystals are covered with cold 70 per cent. alcohol, and repeatedly digested with excess of barium carbonate until crystals of herapathite are no longer deposited when a portion of the solution, made acid with a little oxalic acid, is allowed to evaporate spontaneously. The liquid to be tested is mixed with alcohol and some of the solution, when, if more than a trace of free sulphuric acid be present, a black precipitate of herapathite at once appears. With quantities even as minute as 0·000015 gram of acid, a distinct film of microscopic crystals is formed on evaporating the mixture. The presence of neutral sulphates does not affect the reaction.

According to this test, the solutions of the sulphates of the alkalis (normal), of magnesium, zinc, cadmium, copper, nickel, cobalt, manganese, and thallium, and of the alkaloïds morphine, quinine, strychnine, and brucine, do not contain free sulphuric acid. The acid reaction shown by some of these substances towards litmus is due to dissociation of the unstable metallic salt of the litmus acid formed by double decomposition, an explanation supported by the fact that alkaloïds, brucine for instance, precipitate the hydroxides of zinc, cadmium, copper, manganese, nickel, and cobalt from solutions of these sulphates; solutions of ferrous sulphate and its ammonium and magnesium double salts show an acid reaction, probably due to ferric sulphate. Solutions of chromium, aluminium, glucinum, and ferric sulphates all contain a considerable amount of free sulphuric acid. Solutions of potash alum, ammonium iron alum, and manganese alum contain free acid, but a solution of potassium chrome alum does not do so. A solution of sodium hydrogen sulphate contains free acid.

Jn. W.

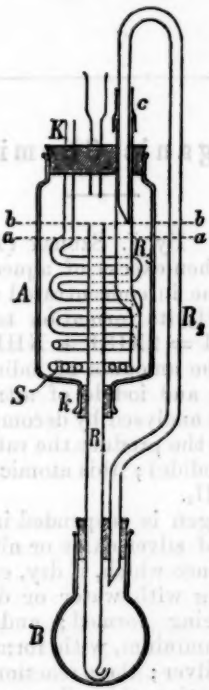
Conditions of Chemical Equilibrium. Part II. By S. Bugarszky (*Zeit. physikal. Chem.*, **12**, 223—229).—The author, in a former paper (this vol., ii, 450), found that the action of potassium bromide on mercuric oxide did not take place according to the law of mass action when conceived as $2KBr + HgO + H_2O = 2KOH + HgBr_2$. He now finds, however, that the reaction is really $4KBr + HgO + H_2O = 2KOH + K_2HgBr_4$, and that the law of mass action is obeyed.

J. W.

Lecture Experiment with the Manocryometer. By L. E. O. de Visser (*Rec. Trav. Chim.*, **12**, 154—156).—A tube of 2 mm. internal diameter, with walls 6 mm. thick, is sealed off at one end and drawn out to a capillary at the other, the whole being about 15 cm. long. This tube is immersed in pure acetic acid and filled by alternately exhausting and admitting air over the acid. The tube is now inverted and the capillary end is plunged into the acetic acid, the wide portion

being cooled by wrapping it in cotton wool on which ether is dropped. The contents solidify with considerable diminution of volume, fresh acid being sucked up. The greater portion of the acid having solidified, the capillary is withdrawn from the acid, and the cooling is continued until air has entered the capillary, which is then sealed off. The tube is now ready for use, and is suspended in a beaker of water, the temperature of which is gradually increased. Acetic acid melts at 16·6° at the ordinary pressure, but when thus confined in a closed space it greatly increases the pressure as it melts, so that the freezing point of the remaining solid is raised. The author has succeeded in raising the freezing point as high as 40°, corresponding with a pressure of about 100 atmospheres. The tubes, when they break, do not explode, but merely crack lengthwise. J. W.

New Extraction Apparatus. By C. T. L. HAGEMANN (*Ber.*, **26**, 1975—1977).—The apparatus figured below has been devised by the author for extracting liquids (aqueous solutions) with solvents. The vessel *A* is charged as far as the dotted line *aa* with the solution to be extracted. The extracting agent (usually ether) is placed in the



flask *B*, which is heated on a water bath; its vapour passes upwards through the tube R_2, into a glass spiral *S*, which is pierced above and sideways with small holes by which the vapour escapes and passes

through the solution to be extracted. It condenses and forms a layer on the upper surface of the solution; when the layer is above *bb*, it flows back into the flask *B* through the tube R_1.

In order that the solution in *A* may not become heated to the boiling point of the ether, which causes violent bubbling of the entire liquid, so that a portion of the aqueous solution is sometimes carried over into the flask *B*, it is necessary to employ a cooling worm, *K*; a reflux for the ether is, however, unnecessary. The ether should be kept in gentle ebullition, and to ensure this, pieces of unglazed porcelain are introduced into the flask *B*.

When using the apparatus with extracting agents heavier than water (chloroform, for example), the spiral *S* is placed in the upper portion of the solution, and above the latter is arranged a condenser. A wider tube, open at both ends, is then placed over the tube R_1, and before commencing the experiment, a small quantity of the extracting agent is poured on to the bottom of the vessel *A*. The vapour of the extracting agent condenses in drops which fall through the solution and collect at the bottom of *A*. The extracting agent rises in the space between the two tubes just described until it overflows through R_1 into the flask *B*. A. R. L.

Inorganic Chemistry.

Iodide of Nitrogen. By J. Szuhay (*Ber.*, **26**, 1933—1945).—The compound formed when excess of aqueous ammonia is added to a strong solution of iodine in concentrated aqueous potassium iodide has the composition NHI_2, its formation taking place according to the equation $3NH_3 + 4I = 2NH_4I + NHI_2$. This was ascertained by finding the ratio of the amounts of iodine, contained respectively in the ammonium iodide and iodide of nitrogen, formed to be 1 : 1. The latter substance was analysed by decomposing it with sulphurous acid, and determining in the product the ratio of nitrogen (present as ammonia) to iodine (as iodide); this atomic ratio is 1 : 2, corresponding with the formula NHI_2.

When iodide of nitrogen is suspended in water, and treated with an ammoniacal solution of silver oxide or nitrate, a compound $NAgI_2$ is formed, a black substance which, if dry, explodes when heated. It is decomposed by boiling with water or dilute acids, silver iodide, iodine, and nitrogen being formed; and is reduced by sodium amalgam or metallic aluminium, with formation of ammonia, hydriodic acid, and metallic silver; these reactions were used to determine its composition. By treating this silver compound with a soluble cyanide, the metal of the latter can be made to replace the silver; the resulting substances are not well characterised, but can be reconverted into the silver compound. C. F. B.

Existence of Nitrous acid in Aqueous Solution. By L. MARCHLEWSKI (*Zeit. anorg. Chem.*, **5**, 88—91).—The author argues that if an aqueous solution of N_2O_3 is a conductor of electricity, it can only be so by virtue of the presence of nitrous acid, there being H and NO_2 ions in the solution. Liquid nitrous anhydride, made from arsenious acid and nitric acid (sp. gr. 1·35), is introduced into a pipette, provided with a stopcock on its stem; the pipette is ground into the neck of a separating funnel, which has two electrodes sealed in its side in such a position that the point of the pipette is just between them. The funnel is full of water, and the liquid is forced into it by a stream of cold water, introduced through the stem of the pipette. It is noted that the solution allows a current from four Daniell cells to pass, and analysis of the liquid withdrawn through the stopcock of the separating funnel indicates that only nitrous acid can be present. The author is satisfied that nitrous acid can exist in aqueous solution, and that there is thus no ground for doubting its existence in dilute nitric acid (compare Armstrong, Proc., 1893, 151).

A. G. B.

Decomposition of Gaseous Hydrogen Phosphide. By D. M. KOOIJ (*Zeit. physikal. Chem.*, **12**, 155—161).—The author has made observations on the rate of decomposition of gaseous hydrogen phosphide at different temperatures, and finds the temperature variation of the constant of velocity k to be expressible by means of an equation of the form $\log k = A/T + B \log T + C$, as theory predicts.

Temp.	k.	k (calc.).
512°	0·0081	(0·0081)
446	0·0025	(0·0025)
367	0·00067	0·00061
310	0·00021	(0·00021)

J. W.

Hexametaphosphates. By H. LÜDERT (*Zeit. anorg. Chem.*, **5**, 15—41).—The following salts were prepared by double decomposition between the salts of the metals and the sodium hexametaphosphate obtained by heating sodium ammonium hydrogen phosphate:—(*a*) As flocculent precipitates, $Ag_6P_6O_{18}$; $Pb_3P_6O_{18}$; $Ba_3P_6O_{18}$; $Sr_3P_6O_{18}$; $Hg_6P_6O_{18}$. (*b*) As gelatinous substances, $Cu_3P_6O_{18}$; $Ca_3P_6O_{18}$; $Mn_3P_6O_{18}$; $Fe_3P_6O_{18}$; $Ni_3P_6O_{18}$; $Hg_3P_6O_{18}$.

A. G. B.

Sulphides of Phosphorus. By A. HELFF (*Zeit. physikal. Chem.* **12**, 196—222).—Observations of the boiling point of carbon bisulphide containing various proportions of sulphur and phosphorus in solution show that no combination between these two substances takes place at the temperature of the boiling solvent. The melting point of mixtures of phosphorus and sulphur is a linear function of the concentration, which shows that the two liquid sulphides of phosphorus, P_4S and P_4S_2, are merely solutions of sulphur in phosphorus. The molecular weight of sulphur dissolved in phosphorus, as determined from the depression of the freezing point, agrees very nearly with the formula S_8.

By heating 4 atoms of red phosphorus with 3 atoms of sulphur, the author obtained only one substance, P_4S_3; but by heating the elements together in the proportion of 2 atoms of red phosphorus to 3 atoms of sulphur, two sulphides of phosphorus were obtained, P_4S_7 with a small quantity of P_4S_3. The substance P_3S_8 was formed when the elements were heated together in the theoretical proportions. When 5 atoms of sulphur were heated with somewhat more than 2 atoms of red phosphorus, only the compound P_2S_5 was obtained. The author thus concludes that the following substances are the chemical compounds of phosphorus and sulphur: P_4S_3, P_4S_7, P_3S_8, and P_2S_5.

J. W.

Sublimation of Arsenic. By J. W. Retgers (*Zeit. anorg. Chem.*, **4**, 403—409).—On heating arsenic in a glass tube closed at the lower end, a sublimate is obtained consisting of several parts. Arsenious anhydride condenses on the part of the tube furthest from the flame; immediately below this is deposited a velvety-black, perfectly opaque ring of arsenic, which is usually described as consisting of amorphous arsenic. This ring is followed by a brown, transparent deposit, separating it from a silver-white sublimate of metallic lustre; the latter consists of ordinary, hexagonal arsenic, the crystals being fairly large. Cubic crystals of arsenious anhydride are observed in all parts of the sublimate; they exhibit the octahedron form, and very rarely the triakisoctahedron. The so-called amorphous arsenic is not really amorphous; the thinner parts of the deposit under a very high power are seen to consist of a number of isolated points which reflect light. It is therefore crystalline, and the crystals probably belong to the cubic system; many unsuccessful attempts were made to obtain larger crystals for microscopic examination. The brown deposit separating this from the sublimate of hexagonal arsenic seems not to have been previously noticed; it is transparent and quite amorphous, is dissolved by boiling water, and consists of an oxide of arsenic, probably the suboxide of Berzelius. A deposit of similar appearance to this is obtained by condensing the flame of hydrogen which has been passed over heated arsenic on cold porcelain; this deposit, however, probably consists of Janowsky's solid arsenic hydride, AsH_2 or As_2H_4. It dissolves in methylenic iodide, xylene, and concentrated potash, and is immediately oxidised to the metallic state by gold chloride, but not by stannic or mercuric chloride. The hydride and the suboxide are easily distinguished by their behaviour towards ammoniacal silver solutions; the former immediately reduces the solution with deposition of metallic silver, whilst the suboxide only becomes reduced after some time. No liquid could be found which acts simply as a solvent of metallic arsenic. Even in the finest state of subdivision arsenic is quite opaque; all observations of yellow or brown transparent arsenic are merely due to confusion with oxide or hydride. W. J. P.

Boron Carbide. By O. Mühlhaeuser (*Zeit. anorg. Chem.*, **5**, 92—93).—This compound is produced by heating a mixture of boric anhydride and carbon in the electric furnace. The graphite-like mass is heated in a platinum crucible for 5½ hours, powdered, boiled with hydrochloric acid, filtered, washed, again boiled with hydro-

chloric acid, and finally treated with hydrofluoric and sulphuric acids. Analysis shows it to have the formula BC or B_2C_2. It is a black powder, having much the same properties as graphite. At a high temperature it becomes soft, and at a very high temperature it melts. It burns with difficulty in oxygen. It is insoluble in nearly all the usual solvents, but is decomposed by fusion with alkalis.

A. G. B.

Behaviour of Charcoal with Halogens, Nitrogen, Sulphur, and Oxygen. By W. G. Mixter (*Amer. J. Sci.*, **45**, 363—379).—Hydraulically-compressed sugar charcoal containing 0·13 per cent. of hydrogen and 0·04 per cent. of ash absorbs about 4 per cent. of chlorine at a red heat, and does not give it up in a vacuum at that temperature. The chlorine cannot be displaced by nitrogen, but can be removed by hydrogen. At the ordinary temperature, little or no chlorine is absorbed. Bromine and iodine are less easily absorbed, and more easily lost. Lamp-black absorbs more chlorine, and both charcoal and lamp-black lose it at the temperature at which porcelain softens. Gas carbon, graphite, and diamond are not affected by chlorine. Charcoal, after ignition in hydrogen chloride, contains 0·26 per cent. of chlorine. Chlorine seems to act with most energy on those forms of carbon which are contaminated with hydrogen. The form in which it is combined is uncertain; nothing is extracted from the product by chloroform, benzene, alcohol, or ether.

Both lamp-black and charcoal absorb nitrogen when heated in a stream of that gas, and do not give it up on heating. The nitrogen exists probably in the form of cyanogen, since that substance is absorbed readily by charcoal at a red heat, yielding a product which, like those obtained by the direct action of nitrogen, yields ammonia when heated in a current of steam. Charcoal also absorbs nitrogen from nitrous and nitric oxides. Animal charcoal, albumin, and uric acid all leave a highly nitrogenous residue when ignited in a closed vessel.

Charcoal absorbs sulphur when heated to a red heat in sulphur vapour or carbon bisulphide. The sulphur is entirely removed by hydrogen, and is practically given up at a red heat. Filter paper soaked in carbon bisulphide and heated in sulphur vapour absorbs nearly its own weight of the latter. The compound so formed does not yield sulphur to carbon bisulphide or boiling aqueous potash.

Hard charcoal requires to be heated to a very high temperature before it will burn in dry oxygen.

Jn. W.

Action of Aqua Regia on Carbon Bisulphide. By Schlagdenhauffen and Bloch (*J. Pharm.* [5], **28**, 241—242).—Excess of aqua regia is distilled with carbon bisulphide either immediately after mixing or after contact for some hours. Red nitrous fumes and unattacked carbon bisulphide first pass over, followed by a very volatile substance, which can be condensed by using a freezing mixture of ice and salt; it proves to be the trichloromethylsulphurous chloride of Kolbe, $SO(OCCl_3)Cl$; it is more readily prepared by this method than by Kolbe's process. The acid residue contains sulphuric acid.

W. T.

Molecular Weight of Potassium Persulphate. By G. Bredig (*Zeit. physikal. Chem.*, **12**, 230—233).—Whilst freezing point experiments indicated $K_2S_2O_8$ as representing the molecule of potassium persulphate, the electrical conductivity gave numbers nearly agreeing with those obtained by Ostwald for potassium perchlorate, which is represented by the molecular formula $KClO_4$. The author points out that Ostwald's determinations were somewhat inaccurate, and that the conductivity experiments also correspond with the formula $K_2S_2O_8$.

J. W.

Double Halogen Compounds of Arsenic with Cæsium and Rubidium; Compounds of Arsenic Trioxide with the Cæsium, Rubidium, and Potassium Haloïds. By H. L. Wheeler (*Amer. J. Sci.*, [3], **46**, 88—98).—The author has described the chemical properties and crystallographic condition of 12 new arsenical compounds containing a halogen and also cæsium or rubidium, of the types $3RbCl,2AsCl_3$ and $RbCl,As_2O_3$. A potassium compound of the formula As_2O_3,KI has also been obtained.

These double haloïd salts are prepared by dissolving arsenic trioxide in strong hydrochloric, hydriodic, or hydrobromic acid, and adding the required proportion of the metallic haloïds, also dissolved in one of the said acids. Excess of one or the other of the constituents has, however, no effect on the composition of the product obtained. The double salts gradually crystallise out.

The oxy-compounds are obtained by making use of but very weak acid solutions. As might be expected, they are also formed by moistening the double haloïds with water. Strong haloïd acids reconvert them into double haloïds.

L. de K.

Incomplete Oxidation of Aluminium. By Pionchon (*Compt. rend.*, **117**, 328—330).—When aluminium is heated in the flame of an oxyhydrogen blowpipe supplied with comparatively little oxygen, it burns brilliantly, and is converted into a dark grey powder which dissolves in hydrochloric acid with evolution of hydrogen and formation of aluminium chloride, whilst a residue of aluminium oxide is left. Estimations of the volume of hydrogen evolved, the quantity of aluminium chloride formed, and the weight of the insoluble residue show that the greyish product of the regulated combustion of aluminium in the oxyhydrogen blowpipe consists of a new oxide of aluminium mixed with small quantities of unoxidised metal and alumina. The new oxide has the composition Al_4O_7 or $Al_2O,3Al_2O_3$.

C. H. B.

Note.—In his presidential address to the Chemical Section of the British Association at Nottingham, Emerson Reynolds pointed out that analytical and other data indicate the probable presence of partially oxidised aluminium in certain silicates.

C. H. B.

Isomorphism amongst Anhydrous Alums. By T. Klobb (*Compt. rend.*, **117**, 311—314).—When chromium oxide, chloride, or sulphate is fused with ammonium sulphate, the double sulphate $Cr_2(SO_4)_3,3(NH_4)_2SO_4$ is first formed, and crystallises in pale green,

microscopic, acicular prisms, which become rose-coloured when heated. It is insoluble in cold water, and is but slightly attacked by boiling water and dilute acids and alkalis. It remains unaltered at 350°, but at a red heat it decomposes, and a residue of chromic oxide is left.

If the fusion with ammonium sulphate is prolonged, anhydrous chromium ammonium alum is obtained in pale green, microscopic, hexagonal plates, which are not affected by boiling water, acids, or alkalis. A boiling solution of potassium hydroxide of sp. gr. 1·3 dissolves the salt very slowly. Water containing chromous chloride or stannous chloride does not dissolve it. At 350°, the salt becomes rose coloured without any change of composition, but at a bright red heat it is completely decomposed.

When chromium potassium alum is fused with ammonium sulphate, a mixed alum, $Cr_2(SO_4)_3,SO_4(K,NH_4)_2$, is obtained, isomorphous with the preceding compound.

If an excess of potassium sulphate is added, a salt of the composition $Cr_2(SO_3)_3,3K_2SO_4$ is obtained in long, silky, green needles.

Another mixed alum, $Cr_2(SO_4)_3,(NH_4,Na)_2SO_4$, isomorphous with the other two, is obtained by fusing chromium and sodium sulphates with ammonium sulphate.

Lachaud and Lepierre have already described the compounds $Fe_2(SO_4)_3,3(NH_4)_2SO_4$ and $Fe_2(SO_4)_3,(NH_4)_2SO_4$. The former crystallises in prisms, and the latter in hexagonal tables. They differ from the corresponding chromium compounds in being readily attacked by cold water.

By operating in the manner described, it is easy to obtain anhydrous mixed alums of the following types, $(Cr,Fe)_2(SO_4)_3,(NH_4)_2SO_4$; $(Cr,Al)_2(SO_4)_3,(NH_4)_2SO_4$; and $(Al,Fe)_2(SO_4)_3,(NH_4)_2SO_4$. Anhydrous aluminium alum can also be produced, but is difficult to isolate.

All these alums crystallise in hexagonal prisms, and their isomorphism affords further proof of the isomorphism of Al_2O_3, Cr_2O_3, and Fe_2O_3 on the one hand, and of K_2O, Na_2O, and $(NH_4)_2O$ on the other.

C. H. B.

Ferric Phosphate. By E. A. Schneider (*Zeit. anorg. Chem.*, **5**, 84—87).—A solution of ferric chloride was saturated with normal calcium orthophosphate, and the solution dialysed. When the diffusate contained no more chlorine, the ferric phosphate on the dialyser set to a jelly containing ferric oxide and phosphoric anhydride, in the proportion 52·99 per cent. : 47·01 per cent. This hydrogel dissolves in ammonia with a reddish-brown colour, and by dialysing the solution ammonium phosphate is gradually removed. When the hydrogel is treated with potash, the resulting ferric hydroxide retains only 1·25 per cent. of phosphoric acid.

Ferric phosphate dissolves to a considerable extent in a solution of ammonium humate (containing 2·72 grams of ammonia per litre); after five months' digestion, 2 litres of such a solution were found to contain 9·144 grams of ash consisting of Fe_2O_3, 52·21 per cent.; P_2O_5, 45·42 per cent.; and SiO_2, 2·00 per cent. The solubility of ferric phosphate in ferric sulphate is already known.

In concluding, the author points out that the ill effect of reversion in a mineral superphosphate may be much annulled in the soil if ammonium humate be present. A. G. B.

Atomic Weights of Nickel and Cobalt. By C. WINKLER (*Zeit. anorg. Chem.*, **4**, 462—464).—The author suspected that the value lately obtained by him (this vol., ii, 469) for the atomic weight of cobalt might be somewhat too high, owing to the formation of a basic cobalt salt during the determination. He has therefore again determined this atomic weight by causing electrolytically deposited cobalt to act on silver sulphate; silver is then precipitated, and a relation between the equivalents of the two metals obtained. A trace of cobalt is retained by the silver, and may be afterwards estimated and allowed for. Two determinations gave Co = 59·6356 and 59·6164 (Ag = 107·66); these numbers are in close agreement with those previously obtained, so that the author's fears as to the accuracy of the method employed are groundless. W. J. P.

Crystalline Chromium Tungstate. By E. F. SMITH and H. L. DIECK (*Zeit. anorg. Chem.*, **5**, 13—14).—The compound $Cr_2O_3,5WO_3$ is obtained in the form of brown, orthorhombic needles, when equivalent quantities of potassium dichromate and tungstic acid are heated together until the mixture fuses and no more gas is evolved. The crystals are not attacked by aqua regia; they were decomposed for analysis by fusion with sodium carbonate and potassium nitrate. A. G. B.

Action of Gases on Molybdenum and Tungsten. By E. F. SMITH and V. OBERHOLTZER (*Zeit. anorg. Chem.*, **5**, 63—68).—Carbonic oxide and ammonia were found to be without action on these metals at temperatures up to a red heat.

When molybdenum is heated at 150—200° in carbonyl chloride, a liquid sublimate is formed, which solidifies to a reddish-brown, gelatinous mass melting below 100°. The analysis of this product indicates that it is a mixture in equal molecular proportions of $MoOCl_4$ and $Mo(CO)Cl_4$.

A similar treatment of tungsten gives rise to an orange-red sublimate consisting of the oxychloride, $WOCl_4$, and containing carbon, which is left when the oxychloride is resublimed.

A reddish-brown, amorphous sublimate of the formula $Mo_5S_8Cl_9$ was obtained by heating molybdenum to a red heat in sulphur chloride. Tungsten, under similar conditions, yields a red, crystalline sublimate, which is unstable in air, and has the formula $W_2S_7Cl_8$, being regarded by the authors as a compound of $W_2S_3Cl_4$ with $2S_2Cl_2$. A. G. B.

Complex Inorganic Acids. By F. KEHRMANN (*Zeit. anorg. Chem.*, **4**, 465—466).—A polemical paper dealing with Friedheim's criticism (this vol., ii, 472) of the author's work (*ibid.*). W. J. P.

Sulphur Compounds of Thorium. By G. KRÜSS and C. VOLK (*Zeit. anorg. Chem.*, **5**, 75—79).—Neither by heating potassium thorium chloride in hydrogen sulphide, nor by heating thorium oxide

in carbon bisulphide in the manner adopted by Chydenius, could the authors obtain the compounds ThS_2 and $Th_3O_4S_2$, which Chydenius claims to have prepared (*Jahresber.*, 1863, 194). In both cases, the compound produced contains thorium and sulphur in equal atomic proportions, indicating the existence of ThS or ThOS.

A. G. B.

Variety of Gold Purple Soluble in Water. By E. A. Schneider (*Zeit. anorg. Chem.*, **5**, 80—83).—To obtain a solution of this form of gold, an alloy of gold, tin, and silver is treated with concentrated nitric acid, and the resulting black powder is washed with ammonia, whereby a ruby-red coloured solution is obtained. This solution is dialysed until it contains no more ammonia; it is coagulated by dilute acids and salts, and by heating under pressure, but not by alcohol, nor by concentrated sulphuric acid. It contains 0·5800 gram of gold, and 5·4048 grams of stannic oxide per litre; 50 c.c. of the solution gelatinises when evaporated to 3 c.c., but the jelly dissolves again in water. Diluted 10 times, it is still red, and a layer 1 cm. thick allows the red, yellow, and less refrangible rays of the green in the spectrum to pass. Potassium cyanide decolorises the liquid, and causes the separation of stannic acid. When shaken with mercury, the colour of the liquid passes into brownish-red, and the mercury extracts gold. When poured into an excess of strong hydrochloric acid, the solution changes in colour to violet, and yields finely-divided gold on dialysis. This behaviour indicates that the soluble form of purple gold is a mixture of the hydrosols of gold and stannic acid, a conclusion supported by the fact that the addition of a few drops of gold chloride and a reducing agent to the hydrosol of stannic acid produce a purple solution. The presence of the hydrosol of stannic acid is essential to the existence of the hydrosol of gold. The author notes a similar behaviour of silver chloride, which can be obtained in a condition in which it can only be coagulated by acids when silver nitrate is added to a dilute solution of ferric chloride.

The hydrosol of stannic acid is best obtained by pouring a dilute solution of stannic chloride into a very dilute solution of ammonia, and dialysing. The clear liquid contains 5·164 grams of stannic oxide per litre. Its behaviour is similar to that of the purple gold solution described above.

A. G. B.

Mineralogical Chemistry.

Rock Salt from Deésakna. By J. Loczka (*Zeit. Kryst. Min.*, **22**, 82; from *Földtani Közlöny*, **21**, 353—358).—Deésakna is situated in the Hungarian county of Szolnok-Doboka, and the salt mined at this locality is characterised by its extreme purity. The author subjected to analysis a pure, transparent crystal of sp. gr. 2148 with the following results.

Na.	Cl.	H_2O.	Total.
39·41	60·64	0·02	100·07

B. H. B.

Falkenhaynite, a new Mineral of the Wittichenite Group. By R. Scharizer (*Zeit. Kryst. Min.*, **22**, 85; from *Jahrb. d. k.k. Geol. Reichsanst.*, **40**, 433).—A greyish-black, dense ore from Joachimsthal was analysed, and, after deduction of 13·16 per cent. of quartz, 12·77 per cent. of magnesia-bearing spathic iron ore, and 3·66 per cent. of copper pyrites, gave results corresponding with the formula $Sb_2S_3Cu_6$, in which one-quarter of the antimony is replaced by arsenic, and one-fifth of the copper by iron and zinc in the ratio of 5 to 3. B. H. B.

Franckeite, a new Ore from Bolivia. By A. W. Stelzner (*Jahrb. f. Min.*, 1893, ii, Mem. 114—124).—The ore described occurs in the Animas mining district, south-east of Chocaya. Locally it is known as *llicteria*, and is described by Jackowski, a Polish engineer resident in the district, as a mineral unknown in Europe, and as consisting of lead, zinc, tin, and silver. Analysis (by C. Winkler) yielded the following results.

Pb.	Sn.	Sb.	S.	Fe.	Zn.	Gangue.	Total.
50·57	12·34	10·51	21·04	2·48	1·22	0·71	98·87

The mineral also contains about 0·1 per cent. of germanium and 1 per cent. of silver. The formula is $5PbS,2SnS_2,Sb_2S_3$. This new mineral, which is of special interest as indicating the character of the occurrence of tin in the Bolivian mines, and also as containing germanium, is named franckeite by the author in honour of C. and E. Francke, two mining engineers specially interested in Bolivian mining. B. H. B.

Kylindrite. By A. Frenzel (*Jahrb. f. Min.*, 1893, ii, Mem. 125—128).—At the Santa Cruz mine at Poopô, in Bolivia, a new mineral has been discovered. This the author has named *kylindrite* from the cylindrical form in which it occurs. The mineral has a metallic lustre, a blackish-grey colour, a hardness of 2·5 to 3, and a sp. gr. 5·42. Analysis gave the following results.

Pb.	Ag.	Fe.	Sb.	Sn.	S.	Total.
35·41	0·62	3·00	8·73	26·37	24·50	98·63

The formula is therefore Pb_3Sb_2,Sn_6S_{21} or $6PbS,Sb_2S_3,6SnS_2$. The mineral differs both in chemical composition and in physical properties from the two similar sulphur lead salts of tin and antimony, plumbostannite and franckeite. B. H. B.

Artificial Minerals obtained in Chemical Industries. By C. Winkler (*Zeit. angw. Chem.*, 1893, 445—447).—The author describes the occurrence of the following minerals produced artificially.

1. *Iron pyrites*, obtained in the process of recovering sulphur from soda residues. The mineral is cryptocrystalline, and has a sp. gr. of 4·7336. Its composition is as follows.

Fe.	S.	Residue.	Total.
46·33	52·52	1·86	100·71

2. *Gypsum*, obtained in the same process. It occurs in well-developed monoclinic crystals, yielding, on analysis,

CaO.	SO_3.	H_2O.	Total.
32·09	46·56	21·07	99·72

3. *Trona*, obtained in the manufacture of bicarbonate of soda by the ammonia-soda process. It is formed in magnificent, pellucid, monoclinic crystals. As formed in the Ebensee ammonia-soda works, the product has exactly the same composition as natural trona, according to B. Reinitzer, $Na_4H_2(CO_3)_3 + 3H_2O$. The author's analysis leads to the formula $Na_3H(CO_3)_2 + 2H_2O$. B. H. B.

New Natural Phosphates. By A. Gautier (*Compt. rend.*, **116**, 1171—1177).—In a previous paper (this vol., ii, 419), the author pointed out that the bed of concretionary phosphates found in the grotto of Minerva constitutes a new type of phosphorites in which the phosphoric acid is combined with calcium and aluminium. This remarkable deposit furnishes also the bibasic natural calcium phosphate, *brushite*, and a new aluminium phosphate.

Brushite, $PO_4CaH,2H_2O$, has hitherto been found only in a guano rock in the Antilles. The description given by Dana of metabrushite corresponds exactly with the properties of the Minerva brushite. The analyses given by the author are in accord with the formula $2PO_4CaH_2 + 3H_2O$.

Minervite is the name given by the author to the new aluminium phosphate. Its composition, $P_2O_5,Al_2O_3,7H_2O$, approaches that of callainite and gibbsite. B. H. B.

Chondrostibian, a new Swedish Mineral. By L. J. Igelström (*Zeit. Kryst. Min.*, **22**, 43—46).—In January, 1893, the author discovered another new antimony mineral in the Sjö mine, celebrated for its occurrence of the minerals hæmatostibiite, ferrostibian, stibiatite, basiliite, and melanostibian. To this new mineral the author has given the name of "chondrostibian" (*χόνδρος*, a grain, and *stibium*, antimony). The small grains of the mineral occur in barytes, and appear at times to form minute crystals of octahedral form. On analysis, it gave the following results.

Sb_2O_5.	As_2O_5.	Mn_2O_3.	Fe_2O_3.	H_2O.	Total.
30·66	2·10	33·13	15·10	19·01	100·00

The formula is consequently $3R_2O_3,Sb_2O_5 + 10H_2O$, in which R_2O_3 represents Mn_2O_3 and Fe_2O_3. B. H. B.

Descloizite from the Obir. By A. Brunlechner (*Jahrb. f. Min.*, 1893, ii, Ref. 254—255; from *Carinthia*, **2**, 8).—The crystals of descloizite were found in fissures in limestone, associated with goethite. Pseudomorphs of descloizite after vanadinite are also met with. The

results of analysis of these are given by the author. The minerals originally occurring in the fissures were galena, blende, marcasite, and calcite. Subsequently the galena became converted into lead sulphate by the decomposition of the marcasite, the lead sulphate was then converted into vanadinite, and finally descloizite was formed.

B. H. B.

Ettringite and Alabandine from Arizona. By A. J. Moses (*Zeit. Kryst. Min.*, **22**, 16—19).—*Ettringite*, $H_{18}Ca_6Al_2O_{18}(SO_3)_3 + 24H_2O$.—This mineral was found at the Lucky Cuss mine at Tombstone, Arizona, in white, crystalline limestone incrusting fissures and cavities in a silicate of lime and alumina. It resembles a finely fibrous pectolite. Its hardness is somewhat above 2, and its sp. gr. 1·27.

Alabandine.—A deposit of alabandine was found at the same mine. The quantity raised amounted to 50 tons. On analysis, the mineral yielded 36·90 per cent. of sulphur and 63·03 per cent. of manganese. Its colour is dark steel-grey to deep black with an olive-green streak. Its hardness is 3 to 4, and its sp. gr. 4·03. B. H. B.

Idocrase. By F. Pisani (*Jahrb. f. Min.*, 1893, ii, Ref. 252; from *Bull. Soc. fran. min.*, **15**, 47—49).—The author gives the following results of an analysis of idocrase from the Septimer.

SiO_2.	Fe_2O_3.	Al_2O_3.	MgO.	CaO.	Loss on ignition.	Total.
39·0	1·8	14·3	6·7	37·4	0·9	100·1

The mineral forms compact, pale greenish-yellow, laminated masses, having a hardness of 6·5 and a sp. gr. of 3·28. B. H. B.

Peculiar Lava from Northern California. By J. S. Diller (*Jahrb. f. Min.*, 1893, ii, Ref. 338—339; from *Bull. U.S. Geol. Surv.*, **79**, 33).—The author describes a late volcanic eruption in Northern California and its peculiar lava. In the latter, the pyroxene is chiefly hypersthene, monoclinic augite being of rarer occurrence. Scattered through the mass are quartz, felspar, and olivine, and in the groundmass there is a second generation of felspar with globulitic glass. The lava has the following composition.

SiO_2.	TiO_2 + Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
79·49	11·60	0·33	0·49	1·64	0·09	1·52	4·04	0·68	99·88

B. H. B.

Two Turkish Meteorites. By S. Meunier (*Compt. rend.*, **117**, 257—258).—The author has examined specimens of the meteorites recently presented to the Museum of Natural History by Halid Edhem Bey. The first was found in 1873 at Tirnowa, in Roumelia. It is covered with a black crust about a millimetre in thickness. On fracture, a clear, grey mass is presented, characterised by its clastic or fragmentary structure. Its sp. gr. is 3·69. The meteorite belongs to the lithological type designated since 1870 in the Museum collection by the name of *mesminite*.

The second meteorite fell on June 2, 1883, in a forest near the village of Urba. It is uniformly white. It has a sp. gr. of 3·427, and is very finely granular. B. H. B.

Analysis of the Wawilowka Meteorite. By P. Melikoff (*Ber.*, **26**, 1929—1932).—This meteorite fell in June, 1876, at Wawilowka, in the Cherson district. In 100 parts it contains:—

A, decomposed by hydrochloric acid, Fe, 1·79; Ni, 0·93; Co, 0·06; FeS, 6·82; P_2O_5, 0·21; olivine, 55·08.

B, undecomposed by hydrochloric acid, FeO,Cr_2O_3, 0·23; silicate, 34·27.

The metallic iron and nickel are present nearly in the ratio $NiFe_2$; the olivine has the composition $2Fe_2SiO_4,5Mg_2SiO_4$, with some of the Mg and Fe replaced respectively by Ca, K_2, Na_2, and Mn; and the undecomposable silicate belongs to the class $M''SiO_3$. C. F. B.

New Iodine Spring in Austrian Silesia. By M. Gläser and W. Kalmann (*Zeit. angw. Chem.*, 1893, 447—448).—The authors have analysed the water from a salt spring at Roy, in Austrian Silesia, with the following results, expressed in grams per litre:—

CO_2.	SiO_2.	Cl.	Br.	I.	SO_3.	FeO.
0·0885	0·0122	15·1236	0·1025	0·0383	0·0031	0·0285

CaO.	MgO.	Na_2O.	K_2O.	Organic.	Fixed residue.
0·9487	0·4661	11·4684	0·1772	0·1028	25·5080

The sp. gr. at 15° is 1·01809. B. H. B.

Physiological Chemistry.

Exercise and Respiratory Interchange. By W. Marcet (*Proc. Roy. Soc.*, **54**, 42—52).—In three persons, if the excretion of carbonic anhydride fell, the oxygen absorbed rose, and *vice versâ*. In a fourth person, of immature age, the oxygen absorbed and the carbonic anhydride expired rose and fell together.

During exercise (stepping), at first there is an accumulation of carbonic anhydride in the blood; this is next given out in the form of a wave, which is renewed after a certain lapse of time. In two persons, the ratio of carbonic anhydride expired in rest to that expired during exercise was found to be the same, namely, 0·123; but further experiment is necessary before this can be laid down as a general law. As a rule, half an hour's rest was sufficient to bring matters back to the normal condition. W. D. H.

Influence of Sodium Chloride on the Digestibility and Assimilation of Proteïd. By S. Gabriel (*Zeit. Biol.*, **29**, 554—569).—Former experimental work has led to the conclusion that

sodium chloride, like water, is of great use to the organism in promoting digestion and the metabolic phenomena that follow absorption. The present experiments, made on three sheep, are divided into periods during which salt was and was not given. The differences of the numbers in the two periods, although not very striking, yet tend to prove the conclusion just alluded to. W. D. H.

Effect of Salt on Digestion. By E. v. Wolff and J. Eisenlohr (*Exper. Stat. Record*, **4**, 974—976; from *Landw. Jahrb.*, **22**, 605—627).—Stutzer's experiments with artificial digestive fluids on proteïds showed a higher rate of digestibility in presence of salt than without salt.

Experiments were made in which sheep were fed with (1) hay alone; (2) hay and brewer's grains; (3) hay and field beans. Each experiment comprised three periods: the first without salt, the second with 4 grams, and the third with 8 grams of salt in the food of each sheep. Besides determining the coefficient for the proteïn by the difference between the amounts eaten and excreted, the metabolic nitrogen was determined in the fresh fæces with acid pepsin solution, and in the air-dry fæces with both pepsin and pancreas solutions. The digestibility of each ration was determined by Stutzer's method. The results failed to show any increase in amounts digested in presence of salt. Experiments with a horse gave similar results.

There is, however, no doubt that salt has a good effect on the general condition of animals and, in some cases, on digestion; as, for instance, when there is a deficiency of hydrochloric acid in the digestive juice. N. H. M.

Digestibility of Milk and Bread. By A. Magnus-Levy (*Pflüger's Archiv*, **53**, 544—560).—The experiments carried out on L. Zuntz, æt. 16, consisted in analysing the diet (milk, and then milk with bread and butter) and the excreta. This simple diet appears to be very well used, and the loss by putrefaction is insignificant. Bunge states that those who do not take alcohol make better use of their food than others. The subject of the present experiments was an abstainer, and the results do not altogether confirm Bunge's statement, although they are not very conclusive. W. D. H.

Influence of Light on Metabolic Processes. By L. Graffenberger (*Pflüger's Archiv*, **53**, 238—280).—The principal change produced in animals by the absence of light is an accumulation of fat. This, however, is not strictly proportional to the duration of the darkness.

The assimilation of nitrogen, the digestion coefficient, the formation of liver glycogen, and the relation of water to solids in the body are not affected.

The only other results of darkness noted were a lessening of the quantity of blood and of hæmoglobin, and, if the deprivation of light were very prolonged, the development of bony tissue and of the liver was delayed. In developing animals, the heart and muscular tissues were relatively heavier under the influence of darkness.

W. D. H.

Urea in the Blood of Birds. By A. Garrod (*Proc. Roy. Soc.*, **53**, 478—484).—Urea occurs in birds' blood in quantity approximately equal to that in mammalian blood. The author has previously insisted that the kidneys, not the liver and spleen, form the situation where uric acid is formed. He considers that the discovery of urea in birds' blood, and the absence of uric acid there, lends support to this contention. If so, nitrogenous metabolism is practically identical in both birds and mammals: in mammals, the urea leaves the body as such; in birds, synthetic processes in the kidney lead to its conversion into ammonium urate, in which form it is excreted. W. D. H.

Diastatic Ferment in Blood. By M. Bial (*Pflüger's Archiv*, **53**, 156—170).—The saccharifying power of human blood is less than that of some other animals. The products are dextrin and dextrose. The blood has also the power of changing maltose into dextrose. In the new-born child, the saccharifying power is weak or absent, and the same is true also for newly born lower animals. W. D. H.

Glycogen. By W. Saake (*Zeit. Biol.*, **29**, 429—483).—The observation of Langley and others, that glycogen occurs in the body in the presence of some vehicle of proteïd-like nature, is confirmed by microchemical investigation of various glycogen-containing cells of adult and fœtal organs. The comparison of hæmoglobin in its vehicle, the stroma, is made. The vehicle, however, is not ordinary albumin, for although it is coagulated by alcohol, it swells in water without dissolving, and is not coagulated by trichloracetic acid.

Fraenkel's method for the preparation of glycogen is criticised; and still more so are his views that the glycogen is actually in combination with proteïd in the body. Mechanical admixture is considered sufficient to explain all his conclusions. W. D. H.

Absorption from the Stomach. By J. Brandl (*Zeit. Biol.*, **29**, 277—307).—Tappeiner (*ibid.*, **16**, 497) obstructed the pylorus in dogs by a bladder inserted through a fistula, and found that an aqueous solution of chloral hydrate did not produce narcosis. If, however, the surface of a small amount of the duodenum were allowed to have absorptive play also, narcosis soon set in. An alcoholic solution of the same substance was, however, rapidly absorbed by the stomach, and produced the usual narcosis. Quantitative experiments with sugar solutions showed that the stomach has little or no absorptive power for aqueous solutions, whilst the presence of alcohol increases its absorptive activity. v. Anrep (*Du Bois Reymond's Archiv, Physiol. Abth.*, 1881, 504) found the absorption in the stomach greater than Tappeiner stated. It is suggested, and the present experiments confirm the suggestion, that this is explained by the fact that he used solutions of greater concentration that Tappeiner did.

The present experiments, all made on one dog, relate to sugar, peptone, and sodium iodide; in all cases increase of concentration led to a stimulation of the process of absorption, and the consequent disappearance from the stomach of a larger amount of material. In all cases also the presence of the solution led to a large secretion from

the gastric walls, usually in excess of the fluid administered. This still further diluted the substance, which, nevertheless, is readily absorbed by the intestinal wall, where there is no necessity for great concentration in order that absorption may occur.

Further, all these effects are increased by alcohol. Alcohol does not stand alone here, but other stomachic stimulants, such as sodium chloride, mustard oil, pepper, oil of peppermint, and orexine hydrochloride act similarly. Bitters do not produce the effect. The presence of colloïd substances, like starch and gum, enormously diminishes the absorption. W. D. H.

Secretion and Absorption in the Small Intestine. By F. Voit (*Zeit. Biol.*, **29**, 325—397).—The experiments were made on dogs, and the first series confirm the observation of Herrmann that isolated loops of intestine contain after a time fæcal-like masses derived in large measure from the secretion of the intestinal wall. On an ordinary diet also very largely, and on a flesh diet almost exclusively, are the fæces passed of similar origin. The same occurs during hunger, and food only slightly increases the amount of fæces passed. The large digestive glands (liver and pancreas) have scarcely any part in the process. By giving large quantities of flesh, the nitrogen in the fæces is increased; but here, again, it is not the nitrogen of undigested food, but an increase in the nitrogen of the intestinal juice. The ash, however, of flesh is not so well absorbed if given in large amounts. The fæces of hunger contain not unimportant quantities of fat (compare "Physiology of Starvation," this vol., ii, 477).

The second series of experiments relates to the absorption of calcium salts. The greater part of these salts, after a diet containing them in large quantity, comes from the food direct. Comparison with the fæces of hunger shows that a certain amount also is secreted in the intestinal juice, but this is only very slightly increased by food rich in lime. The bile plays here only an insignificant part. Another part of the absorbed calcium salts leaves the body in the urine. The amount of calcium salts absorbed is increased with difficulty by tricalcium phosphate, by milk or by injection of proteïd-calcium combinations into the intestine. Injection of 1 to 3 per cent. solutions of calcium chloride are more efficacious, but are contra-indicated by the fact that they produce pathological changes in the mucous membrane.

The third and last series of observations relates to iron, which was given in the form of *liquor ferri albuminati*, oxyhæmoglobin, and ferric citrate. The absorption of these substances was found to be very low. The small quantities which appeared to be absorbed left the body partly in the urine, but chiefly in the intestinal juice. The bile hardly comes into account in this connection; the little iron it does contain appears to be absorbed by the intestinal wall. It is calculated that the small amount of iron absorbed leads only to an output in the intestine of a few milligrams daily. The greater part of the iron in the fæces comes directly from that administered.

W. D. H.

The Phosphates of Milk. By Duclaux (*Exper. Stat. Record*, 4, 978; from *Ann. Inst. Pasteur*, 1893, 2—17).—Phosphates exist in milk

in a soluble form, tricalcium phosphate and sodium phosphate, and in an insoluble form, phosphates of iron, aluminium, magnesium, and calcium. The insoluble portion contains about twice as much lime and calcium phosphate as the soluble portion.

"Phosphate milk," a milk in which the phosphates are supposed to have been increased by feeding calcium phosphate, contains no more phosphates than other milk. Analyses of milk from various sources showing the total lime as calcium phosphate, the excess of phosphoric acid, mostly combined with aluminium, iron, magnesium, and sodium, and the other mineral constituents are given. The different results agree closely, so that any addition of either soluble or insoluble phosphates could be detected from the change in the relation of soluble to suspended phosphates. N. H. M.

Effect of Work on the Excretion of Phosphoric acid. By F. Klug and V. Olasavsky (*Exper. Stat. Record*, **4**, 976; from *Arch. Ges. Physiol.*, **54**, 21—26).—Preysz (*Ungar. Arch. Med.*, **1**, 38) found that the phosphoric acid excreted by a man was increased by muscular work. The authors confirmed this with experiments on a dog. During 10 days of rest, the average daily amount of phosphoric acid excreted in the urine of the dog was 0·3175 gram. When put to hard work, the amount increased to 0·57 gram. On the next day, it fell to 0·28 gram. The increase is probably due, to a great extent, to the lactic acid formed in the muscles during work; perhaps, in a smaller measure, to carbonic anhydride. Water containing lactic or carbonic acid will dissolve much more phosphoric acid from fresh meat and bones than pure water. Moreover, by adding lactic acid to a dog's food, the phosphoric acid in the urine was distinctly increased. N. H. M.

Transformations of Arsenious Anhydride in the Organism. By D. Vitali (*L'Orosi*, **16**, 73—87; compare following abstract).—The author gives a summary of our knowledge concerning the changes undergone by arsenious anhydride in the organism. Neither arsenic acid nor arsenious acid combines with albumin to form albuminates. By experiments on dogs, the author confirms the observation that arsenious anhydride is converted by the organism into arsenic anhydride, which then passes into the urine; the arsenic acid is not found free in the urine, but in a state of combination, and probably displaces phosphoric acid in phosphoglyceric acid; the latter being a decomposition product of lecithin, it would seem that arsenic can replace phosphorus in this. This is confirmed by an examination of the liver and brain of a dog to which considerable quantities of arsenious anhydride had been administered. W. J. P.

Absorption and Physiological Action of Arsenic Trisulphide. By D. Vitali (*L'Orosi*, **16**, 145—149).—Pure arsenic trisulphide is not poisonous; the commercial product, however, contains more or less arsenious anhydride, which is, of course, very poisonous. The administration of considerable quantities of the trisulphide to a dog is attended by an improvement in the health of the animal: the explanation of this lies in the fact that only a small proportion of the

sulphide passes into the urine as arsenic acid. The effect is hence the same as that of administering very small doses of the latter substance; this, as is known, is beneficial.

The author again confirms his conclusion (compare preceding abstract) as to the oxidation of arsenious anhydride in the animal organism. In searching for arsenic acid in the urine of the dog, magnesia mixture should be added, and the precipitated ammonium phosphate and arsenate reprecipitated from its acetic acid solution until colourless; on then applying Marsh's test, unmistakable evidence of the presence of arsenic acid is obtained. W. J. P.

Physiological Action of the Two Isomeric Ethylic Thiocarbamates. By W. J. Smith (*Pflüger's Archiv*, **53**, 481—490).—These two isomerides differ in the position of the sulphur in the molecule. From experiments on dogs and frogs, it was found that practically none or only traces of either pass into the urine as such; a part of the sulphur is excreted as sulphuric acid. The nitrogen output is also increased. The symptoms produced are of the nature of paralysis followed by death; and the more poisonous of the two compounds was that in which the sulphur was combined as CS·OEt, not as CO·SEt. W. D. H.

Physiological Action of Organic Oximides. By H. W. Pomfret (*Proc. Roy. Soc.*, **53**, 398—404).—The action of fatty aldehydes on voluntary muscle is to produce contracture and loss of irritability; on nerves, a primary slight increase of irritability becomes more evident as the series is ascended; on the spinal cord, there is a primary increase, followed by a secondary depression; as a rule, vessels are constricted. All tend to slow the heart, but show a primary tonic action. As the atomic weight of the aldehyde increases, weaker solutions are required to show the tonic effect, and the arrest in diastole is more quickly reached. The corresponding aldoximes reflect the combined action of a nitrile and aldehyde, becoming more toxic as the series is ascended.

Aromatic aldehydes have the same type of action, but are more powerful, and the corresponding aldoximes scarcely differ at all from these.

Acetoxime and isonitrosoacetone, in their action, closely resemble the fatty aldoximes.

Acetone differs from the aldehydes chiefly in causing no contracture. Its effect on vessels and heart is very slight. The COH group is believed to be closely associated with contracture, a phenomenon stated to be due to irritation of the end plates. It is prevented by curare. Experiments on the oxidation of acetoxime and isonitrosoacetone led to the detection of an aldehyde (pyruvic aldehyde). If this occurs in the tissues, it will account for the contracture they produce. W. D. H.

Physiological Action of Sugar. By V. Harley (*J. Physiol.*, **15**, 139—161; *Proc. Roy. Soc.*, **54**, 179—186).—A full account of experiments previously recorded in brief (see this vol., ii, 543). W. D. H.

Physiological Action of Sugars. By M. CREMER (*Zeit. Biol.*, **29**, 484—553).—The paper contains lengthy dissertations on the glycogen question, and on the properties of sugars, with references to literature. There are also experiments recorded on man and animals, relating to the question of whether glycogen originates from different kinds of sugar given by the mouth, and which of these passes into the urine. The most interesting facts appear to be those relating to the rarer forms of sugar. It is found that d-mannose works undoubtedly in increasing glycogen. It goes more readily into the urine than dextrose or levulose, but not so easily as the pentoses (arabinose, xylose, and rhamnose), or as sorbose. Galactose also appears to increase glycogen in the body. W. D. H.

Physiological Action of Uric acid. By A. HAIG (*J. Physiol.*, **15**, 167—175).—Experiments on the author's own person have led him to the conclusion that uric acid, taken by the mouth, increases the excretion of that substance in the urine. W. D H.

Physiological Action of Quinoline, Isoquinoline, and their Derivatives. By R. STOCKMAN (*J. Physiol.*, **15**, 245—248).—Quinoline is a strong antiseptic and antipyretic, depressing the central nervous system. No difference, quantitative or qualitative, could be detected between its action and that of isoquinoline. The two methiodides also acted in precisely the same manner, causing a more paralysing action on the motor nerves than the alkaloïds themselves.

The physiological action of quinaldine (α-methylquinoline), lepidine (γ-methylquinoline), $\alpha\gamma$-dimethylquinoline, orthotoluquinoline, and paratoluquinoline was also investigated.

Tartrate of quinaldine has, on frogs and rabbits, an action similar to that of quinoline, but is somewhat less active; the dimethyl compound is still less active. It would appear, therefore, that the substitution of methyl for hydrogen weakens the depressing action on the nervous system. The other substances act in every respect like quinaldine.

The position of the nitrogen atom or of the methyl group exerts no influence on the physiological action of these substances.

W. D. H.

Dandruff of the Horse. By F. SMITH (*J. Physiol.*, **15**, 162—166).—Dandruff obtained by the grooming of horses consists of epithelium scales, fat, dirt, and hair, together with the secretion of the sebaceous glands. Analysis gave the following results.

Water.....	17·96	
Fat.....	12·40	
Organic matter....	56·22,	containing 1·08 urea
Ash.....	13·42	„ 2·45 silica

The fat resembles lanolin, and is increased by a diet of oats, as compared with one of hay. Cholesterol was obtained in a crystalline form from the organic matter; there is also proteïd present. The ethereal or alcoholic extract is green, especially with a hay diet, and

this is lessened by a diet of oats. Spectroscopic examination of the fluid left little doubt that the green pigment is a derivative of chlorophyll, the proportion of which varies with that in the food. Hay contains the same derivative of chlorophyll, namely, phyllocyanin. The greatest amount of chlorophyll in the food leaves the body in the fæces. None was found in the blood. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Butyl Alcoholic Fermentation and the Butylic Ferment. By M. W. Beijerinck (*Rec. Trav. Chim.*, **12**, 141—153; and *Verhand. Kon. Akad. Wetensch., Amsterdam*, 1893 [2e Sec.], Deel **1**, No. 10).—Normal butyl alcohol is formed during the butyric fermentation of sugar, and also by a fermentation named by the author butylic; it is also found as an accessory product of the assimilation of two other microbes occurring in the soil. That which was believed by Fitz (Abstr., 1882, 1121) to be the butylic fermentation is, in reality, only the butyric fermentation. The two ferments resemble one another, and both belong to a new species of *Granulobacter*, so-called because they contain granulose. *Granulobacter butylicum*, the true butylic ferment, occurs in association with Fitz's ferment, *G. saccharobutyricum*, on the surface of corn grains. The author has, however, found *G. butylicum* alone on certain hulled grains, *Hordeum distichon nudum* and *Hordeum vulgare himalayense*. To study the ferment, these grains are to be recommended, but they must be collected during the summer of the same year. About 20 grams are ground, and the flour made into a paste with 100 c.c. of hot water, so that the temperature of the paste is not higher than 95°, a precaution which it is necessary to observe, as the spores of the butylic ferment are killed by keeping them for a few seconds at 100°. The other organisms are destroyed below 95°. Fermentation is allowed to proceed at 35°; at the end of 48 hours the starch liquefies, gas is evolved, and the odour of butyl alcohol becomes apparent; there are, however, present in this liquid foreign bacteria, whose spores have survived the high temperature, notably the forms known as *Bacillus subtilis;* these have, however, no ill effect on the butylic ferment, which is anaërobic, and grows in the lower portion of the culture liquid. In the event of contamination with the butyric ferment (also anaërobic), the butyl fermentation is arrested. From the crude fermentation, pure cultures are then made in sterilised, faintly acid wort, contained in vessels which can be filled and inoculated without the admission of air; the dissolved atmospheric oxygen is previously removed from the wort by boiling. The fermentation is conducted at 35°, and lasts about 60 hours. The yield of butyl alcohol is about 1—2 per cent. of the flour employed, and the other products of the fermentation are carbonic anhydride and hydrogen; volatile organic acids are quite absent, which dis-

tinguishes it from the butyric ferment. The organism can be precipitated from the liquid by means of ethyl alcohol, the latter being added until the mixture contains 70 per cent. of it; after being dried in the air, the ferment forms a brown, pulverulent substance, which is coloured blue by iodine, and contains about 15 per cent. of water, and (dried at 110°) 25 per cent. of proteïd substances. Preparations have been kept for six years without losing their vitality. The dried, as well as the fresh, organism contains an enzyme "*amylase*," similar to the diastase of malt, the presence of which can be readily demonstrated by its hydrolytic action on starch, maltose, and dextrin, but no glucose is formed. The "amylase" is secreted only on the surface of the bacteria, but they deposit a variable quantity of granulose within the cell. The organism is treated with cold concentrated hydrochloric acid, washed, neutralised, and the granulose, extracted by means of boiling water, is precipitated by alcohol. It seems to be identical with that obtained from potatoes, as it is transformed by the above described "amylase" into maltose and dextrin, and by the maltase of non-germinated grain into erythrodextrin and maltose.

It has been observed that the spores of the butylic bacteria only retain their vitality for three months in the fermented liquids, whilst the bacteria themselves die earlier; the granulose then disappears, which is, doubtless, due to the amylase, as this penetrates the cells of the dead organisms and saccharifies the granulose. The bacteria are, therefore, best preserved in the dry state. The fermentation and propagation of the organism are only possible in the entire absence of oxygen, or when the pressure of this gas is reduced to an extremely small minimum. In the former case, a variety of the organism results which is denoted by the author the "*clostridium form*"; and in the latter case, a variety denoted the "*oxygen form.*" The "oxygen form" is not easily distinguishable from the *Bacillus subtilis*, is very mobile, and is coloured yellowish-brown, like most bacteria, by iodine; hence it does not contain granulose. If the quantity of oxygen is relatively large, the mobility ceases, and the bacteria becomes more or less filiform; finally, when the pressure of oxygen exceeds the maximum limit, all multiplication and fermentation is arrested.

The butylic fermentation always commences with a period in which the "oxygen form" predominates; the composition of the evolved gas is $CO_2 + 4H_2$. After the last trace of oxygen has disappeared, and the "clostridium form" appears, the development of hydrogen diminishes and that of the carbonic anhydride increases, until, at the end of the fermentation, the composition of the evolved gas is $5CO_2 + H_2$. The principal phase in this fermentation is characterised by the predominance of the clostridium form. The spindles have at one extremity an ellipsoïdal cavity, enclosing a spore of the same shape. These spores may be heated for some seconds at 100° without losing their vitality. It is, also, at this stage of the fermentation that the granulose accumulates and the secretion of the "amylase" is most active. The author believes that the obligatory and optional anaërobic fermentation depends on the presence of easily reducible substances; when these fail, life is impossible or possible

only under specially favourable conditions of nutrition and in presence of oxygen under low pressure. The anaërobic cultures of the ferment are best obtained at a temperature of 10—15° with solutions of glucose or starch in water, to which 0·05 per cent. of the potassium hydrogen phosphate and 1 per cent. of peptone have been added.

The third form of the anaërobic fermentation, designated by the author "*temporary anaërobiose*," and which occurs in ordinary alcoholic fermentation, is characterised by the necessity of renewing the free oxygen after the multiplication of a small number of cells (20—30 in the case of yeast), and, doubtless, depends solely on a reserve of this element in the protoplasm of the cell. This last circumstance explains, to a certain degree, why the reducing function, which is never wanting in any obligatory or optional anaërobic fermentation, is absent in the case of fermentation by yeast.

The production of gas may be considered as the principal characteristic of fermentation proper, and the biological significance of this is the mechanical transportation of the microbes towards the surface of the liquid, where they gain access to oxygen. Hydrogen, the formation of which requires great expenditure of energy, is, on account of its low density, of great importance for this purpose.

A. R. L.

How are Nodule-bearing Leguminosæ enabled to utilise Free Atmospheric Nitrogen? By F. NOBBE and L. HILTNER (*Landw. Versuchs-Stat.*, **42**, 459—478).—The results of experiments hitherto made on the fixation of free nitrogen seem to indicate that the albumen of the bacteroïds, which finally benefits the plant, is produced in a process of life of the bacteria, so that the nodules might be compared with insectivorous plants. But there was no proof that the *Bacillus radicicola* could fix nitrogen to any extent, the small gain noticed by Beyerinck (Abstr., 1892, 1019) being quite incomparable with the enormous gains observed in leguminous plants under the influence of the symbiosis. Bacteria are converted into bacteroïds at an early stage, but the resorption of the bacteroïds does not take place until long after nitrogen assimilation has commenced; moreover, the total nitrogen of the nodules would by no means account for the very large amounts found in the plants.

The results of the authors' experiments now described, when taken together, show that the assimilation of nitrogen is connected with the production of bacteroïds. In the first experiments (the summer of 1891), peas were infected with pure cultivations of nodule bacteria. Nodules were formed unusually quickly, but the infected plants were even less vigorous than those which were not infected. The nodules were found to contain immense numbers of unchanged bacteria, but no bacteroïds. Early in 1892, a similar experiment gave the usual result, production of nodules and increased growth; and the same result was obtained in a third experiment commenced 12th July. A fourth experiment, however, made at the end of July, gave results similar to those obtained in 1891. Plants which were seeded, and at the same time received 0·35 gram of nitrogen, had normal nodules, and grew well. Other plants, which were not inoculated, but received the same amount of nitrogen as the first, remained free from nodules,

were vigorous, but produced less growth than the manured and seeded plants. Whilst the third series, which were inoculated, but received no combined nitrogen, showed very little development; there were many nodules, some of which were larger than those of the first series, but they contained unchanged bacteria instead of bacteroïds. In one pot of this series, four of the plants began early in October to show some vigour, and their nodules were in part normal. It is thus seen that a pure cultivation of *B. radicicola* may at one time give rise to nitrogen assimilation, and that the same cultivation may suddenly cause plants to fail, although in this case nodules are produced as in the first. The reason of this is the increased vegetative power of the bacteria through cultivation on gelatin. This is shown by the much more rapid growth on gelatin in the summer than early in the year, and by the quicker production of nodules. The influence of the plant, as regards bacteroïd formation, was obviously lessened by the increased vigour of the bacteria, but increased under the influence of nitrogenous manure. Nodules containing bacteria only were injurious rather than beneficial to the plant. Unchanged bacteria seem to have nothing to do with nitrogen fixation, which only commences with the production of bacteroïds. Under natural conditions, the two factors necessary for the production of abnormal nodules (namely, abnormally vigorous bacteria and soil free from nitrogen) are wanting.

Experiments were next made to ascertain whether the bacteria of all the Leguminosæ belong to one or several varieties. Various plants were grown in soil and in nitrogen-free sand, and infected with pea and with *Robinia* bacteria. *Lupinus luteus* and *angustifolius*, *Acacia Lophanta*, and *Julibrissin* produced nodules only when grown in sand, whilst peas and *Robinia* plants produced nodules both in soil and in sand. In the case of lupins and acacia, the plants are only able to be infected by these bacteria when they have reached the period of hunger. As regards the size of nodules, larger nodules were formed in nitrogen-free sand than in nitrogenous soil. The difference was very marked in the case of *Robinia*. *Robinia* plants were grown without nitrogen, with 10 milligrams of nitrogen, and with 100 milligrams of nitrogen; there was a similar series, but also inoculated. The amount of growth was greatest in the case of the inoculated plant receiving the larger amount of nitrogen; the next in amount of growth was the unseeded plant with 100 milligrams of nitrogen. The growth in the case of the inoculated plant with 10 milligrams of nitrogen was almost as much as the first two, whilst in all the other experiments there was much less growth. A small initial amount of nitrogen is thus practically as effective as a large amount. The large nodules of the seeded plants kept without combined nitrogen contained, besides unchanged bacteria, chiefly bacteria in the first stage of their conversion into bacteroïds; they were 0·5 to 0·9 μ thick to 2·5 μ long. The much smaller nodules of the plants manured with nitrogen contained only bacteroïds, and these were very large, as much as 9 μ long.

Many leguminous plants, especially *Robinia*, yield a greater *final* gain of nitrogen when grown in nitrogen-free soil than in soil sup-

plied with combined nitrogen. This is due to the fact that later in the season the conversion of bacteria into bacteroïds becomes complete, and the large nodules then give rise to an extraordinarily increased growth, much greater than that induced by the smaller nodules formed under the influence of nitrogenous manure. This probably holds good in the case of yellow lupins (Frank, *Landw. Jahrb.*, **21**).

Bacteroïds are formed by the division, without separation, of bacteria. In the first stage, the rod divides in the middle; the two poles are coloured, just like the unchanged bacteria, the intermediate space remaining colourless. This process continues, and branches may be formed. It seems probable from their structure that, in the absorption of nitrogen, the bacteroïds act like lungs; they offer an enormous surface; or they may be more appropriately compared with gills, if Bouquet's theory of absorption of nitrogen dissolved in water should prove to be correct (*Journ. Agr. Pract.* and *Bied. Centr.*, 1891, 424). As bearing on this, it may be mentioned that in the author's experiment with *Robinia*, the plant evaporated 12 litres of water and assimilated 600 milligrams of nitrogen, or 50 milligrams per litre. Water at 10° will only absorb about 20 milligrams of nitrogen per litre; but inasmuch as the experiment was in progress for five months, and it is probable that the water near the nodules would become exhausted as regards nitrogen, Bouquet's theory is worth considering. In water cultures, nodules are much less effective than in soil, and this may be due to the slower absorption of nitrogen than in capillary soil. N. H. M.

Fixation of Nitrogen by Plants. By P. Kossovitch (*Izvéstiya Petrovskoi Selskochozyaistvennoi Akademy*, **15**, ii, 1—32).—The author has made a series of experiments in order to ascertain whether it is the roots or the leaves of plants which are active in fixing free nitrogen. His method consisted in keeping either the leaves or the roots of the experimental plants (peas) surrounded by an atmosphere of oxygen and hydrogen (the other part being exposed to the air), and, after the lapse of 1—3 months, determining the amount of nitrogen in the plant. The soil was sand freed from nitrogen compounds. He considers that his results go to show that, in papilionaceous plants, the free nitrogen which is fixed is chiefly absorbed through the roots; although he does not deny that some may also be fixed by means of the leaves. J. W.

Assimilation of Nitrogen by Plants. By E. Bréal (*Ann. Agron.*, **19**, 274—293).—A number of experiments are detailed by the author from which he draws the following conclusions:—The soils of forests and natural prairies are highly charged with organic matter, forming a medium in which the nitric ferments cannot transform ammonia into nitrate. The vegetation covering these soils is, therefore, obliged to assimilate nitrogen in the form of ammonia.

Grasses, in fact, flourish in nutrient solutions containing nitrogen as ammonia only, quite as well as in those containing the same quantity of nitrogen as nitrate. They even have the power of converting

nitrate into ammonia when a weak solution of nitrate is caused to trickle over them in presence of air and sunlight, and they continue to grow, blossom, and seed, at the expense of the ammonia so produced.

The principal cause of loss of nitrogen by soils, namely, nitrification, being thus very feeble in grass land, such land becomes enriched in organic nitrogen by the operation of the several modes of fixation of atmospheric nitrogen now known to exist.

When grass land is ploughed up, the yield of other crops is by no means proportional to the mass of organic nitrogen accumulated in the soil. No doubt the abundance of insects in pasture soils is one of the causes determining their relative want of fertility; but, in addition to this, the *débris* of the grasses is an absolute hindrance to nitrification; experiment shows that the same soil nitrifies more when unmixed than when mixed with the roots of grasses.

An entire grass crop, ploughed in as manure, augments the nitrification to some extent, but much less than a leguminous crop containing the same quantity of nitrogen.

The hindrance to nitrification is much less when the grass is applied as manure to a rich soil, like garden soil, in which the nitrifying ferments are already abundant, than when it is ploughed in *in situ*. Grass crops ploughed in occasion a loss of nitrogen in the gaseous state. Vegetable matter, ploughed in, acts as a nitrate-reducing ferment; if it is *sterilised* before being mixed with the soil, nitrification is increased. J. M. H. M.

Formation of Citric acid by the Fermentation of Glucose. By C. Wehmer (*Compt. rend.*, **117**, 332—333).—Two moulds have the property of fermenting solutions of glucose, juices of fruits, and other liquids containing sugar, with production of a considerable proportion of citric acid. The spores of these moulds are abundant in the air, and are found in widely separated localities. The moulds themselves form at the surface of the liquid in a somewhat thick layer resembling *Penicillium*, but the organs of reproduction are small and the precise description and definition of the species is very difficult. The author calls the two moulds *Citromycetes*, and distinguishes the two species as *pfefferianus* and *glaber*. C. H. B.

Analyses of California Prunes, Apricots, Plums, and Nectarines. By G. E. Colby (*Exper. Stat. Record*, **4**, 918—921; from *Californ. Stat. Bull.*, May, 1893; compare this vol., ii, 140).—The following table gives the percentage amounts of various constituents in the whole fresh fruit and in the juice.

	In fresh fruit.				In juice.	
	Dry matter.	Ash.	Nitrogen.	Sugar.	Sugar.	Acid.
Prunes.....	22·62	0·49	0·162	15·35	20·00	0·40
Plums.....	22·57	0·54	0·181	12·89	17·97	0·48
Apricots.....	14·84	0·49	0·194	11·10	13·31	0·68
Nectarines.....	21·00	0·50	0·117	14·11	17·17	0·62

The composition of the ash of the whole fruit, (1) French prunes and (2) Royal apricots, was found to be as follows :—

	K_2O.	Na_2O.	CaO.	MgO.	P_2O_5.	MnO_2.	P_2O_5.	SO_3.	SiO_2.	Cl.
1.	63·83	2·65	4·66	5·47	2·72	0·39	14·08	2·68	3·07	0·34
2.	59·36	10·26	3·17	3·68	1·68	0·37	13·09	3·63	5·23	0·45

As regards amounts of minerals removed from soils by different fruits, grapes come first, then figs, oranges third, and prunes, apricots, and plums fourth. This refers to fruit grown in the United States, which differs from European fruit in the amount of ash constituents.

N. H. M.

Chemical Changes in Tobacco during Fermentation. By S. W. Johnson (*Exper. Stat. Record*, **4**, 910—911; from *Conn. State Stat. Rep.*, 1892).—Duplicate samples of upper leaves, leaves lower down on the stalks, and best leaves were selected, and in each case one sample was analysed at once; the other fermented before analysis. In fermenting, there was a loss of 9·7, 12·3, and 9·1 per cent. in the upper, lower, and best leaves respectively, chiefly due in the case of the lower leaves to the evaporation of water, but in the case of the upper leaves to loss of dry matter. The best leaves lost about equal amounts of water and dry matter. The loss of nicotine amounted to over one-third in the upper leaves, less than half in the lower leaves, and less than one-sixth in the best leaves. The upper leaves lost over one-seventh of the nitrogen-free extract, and one-fifth of the ether extract. The best leaves lost chiefly nitrogenous matters other than nicotine and nitrogen-free extract, including the "gum" of tobacco. N. H. M.

Analyses of Tobacco Stalks when cut and after curing. By S. W. Johnson (*Exper. Stat. Record*, **4**, 911—912; from *Conn. State Stat. Rep.*, 1892).—Three lots of four tobacco plants were selected on 22nd August. No. 1 was cut, whilst still unripe, the same day. Nos. 2 and 3 were cut, when ripe, on the 7th September. 1 and 3 were analysed at once, 2 after being cured until 16th October. The following table gives the total amounts of stalks and the constituents in lbs. per acre.

	Total weight.	Dry matter.	Starch.	Dextrose.	Nicotine.	Nitrogen.
1.	9·437	1·279	147	38·0	6·6	25·5
2.	3·438	1·323	171	8·7	?	41·8
3.	9·750	1·328	189	36·0	8·8	32·2

	P_2O_5.	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3 Al_2O_3.	SO_3.	Cl.
1.	5·5	47·8	1·1	11·9	5·6	1·2	6·8	5·6
2.	7·9	54·7	0·9	14·7	6·9	0·7	7·4	6·8
3.	5·8	50·6	1·1	15·4	6·8	1·3	6·3	6·5

The stalks thus gained in nearly every constituent in the period of growth between 22nd August and 7th September. N. H. M.

Swedish Fodder Plants. By A. G. Killgren and L. F. Nilson (*Exper. Stat. Record*, **4**, 971—973; from *Kgl. Landtbruks Akad. Handl.*, **32**, 88—106).—The composition of five phanerogamous and

four cryptogamous plants from N. Sweden was determined. The plants are all used more or less as fodder. The plants analysed were (1) *Alchemilla vulgaris*, (2) *Epilobium alpinum*, (3) *Melampyrum pratense*, (4) *Malgedium alpinum*, (5) *Stellaria graminea*, (6) *Equisetum fluviatile*, (7) *E. palustre*, (8) *Cetraria nivalis*, (9) *Cladonia rangiferina*. The dry matter had the following percentage composition:—

	Ash.	Crude protein.	Ether extract.	Crude fibre.	Nitrogen-free extract.	Nitrogen.	Digested nitrogen.
1.	8·33	13·19	4·13	14·90	59·36	2·11	1·98
2.	11·35	15·43	3·61	13·49	56·12	2·47	2·29
3.	7·89	12·06	1·67	24·07	54·31	1·93	1·14
4.	16·17	14·43	3·43	20·18	45·79	2·31	1·94
5.	5·94	10·88	2·10	24·65	56·43	1·74	1·39
6.	17·54	10·57	1·57	20·09	50·23	1·69	1·40
7.	17·17	15·84	2·46	14·48	50·05	2·53	2·24
8.	0·86	2·17	3·57	2·65	90·75	0·35	0·19
9.	0·59	1·83	1·87	95·71		0·29	0·17

The small amount of nitrogen in the two lichens (8 and 9) is remarkable considering that they form the sole food of the reindeer for a part of the year. The amount of moss which the reindeer would have to consume daily according to the German feeding standards would decidedly exceed the capacity of the animals. The reindeer-moss (9) is used for cattle, whilst the *Cetraria* is mostly fed to sheep. The lichens are treated with hot water and sometimes mixed with barley or oatmeal, and salt before being fed. N. H. M.

Experiments with Ammonium Sulphate and Sodium Nitrate for Barley and Oats. By S. Rhodin (*Exper. Stat. Record*, **4**, 965—966; from *Kgl. Landtbruks Akad. Hand.*, **30**, 142—148 and **32**, 78—82).—Experiments hitherto made in England and Germany on the relative value of ammonium salts and nitrate for potatoes and roots showed that the nitric nitrogen is considerably the more effective. With cereals, the results are, however, conflicting. Whilst Lawes and Gilbert found that 100 lbs. of nitric nitrogen increased the yield of barley and wheat by 50 lbs. of grain and 100 lbs. of straw above the yield obtained by the application of the same amount of nitrogen as ammonia, Maercker, experimenting with barley and oats, and Wagner, experimenting with oats, rye, and other crops, found the value of nitrogen in the two forms to be about the same. In the author's experiments, barley and oats were grown in a heavy clay, rich in potash and phosphates, and supplied with sodium nitrate and with ammonium sulphate. The weather was unfavourable during the two years of the experiment. Taking the average yields, it was found that barley was more benefited by the nitrate than by the ammonia, whilst in the case of oats the ammonia was somewhat more effective than the nitrate. N. H. M.

Manuring Potatoes. By Edler (*Bied. Centr.*, 1893, 657—659).—Comparison of the effects of potash, nitrogen, and phosphorus

manures on the yield and composition of potatoes showed that phosphates alone had no effect whatever on the increase, but rather caused a decrease when employed in conjunction with nitrogen or potash.

Potash in all cases increased the yield, which was still further added to by the action of nitrogen.

Unmanured potatoes contained most dry matter and starch, the percentage thus obtained being closely approached by that found when potash alone was applied.

The author considers that there is an insufficiency of potash and nitrogen in a soil to permit of a full yield of tubers, consequently there must be some assistance; on the other hand, there is enough of phosphates to produce a normal yield, and no further addition of this manure is necessary. E. W. P.

Available Phosphoric acid and the Soluble Potash in Cotton Seed Meal. By M. B. HARDIN (*Exper. Stat. Record*, **4**, 901; from *S. Carolina Stat. Bull.*, Dec., 1892).—In the original paper, tables are given showing the soluble, insoluble, reverted, and total phosphoric acid, and the total soluble potash, in 13 samples of cotton-seed meal. The average meal (with about 7 per cent. of nitrogen) contains nearly 2·5 per cent. of available phosphoric acid and a little more than 1·5 per cent. of soluble potash, corresponding with over 0·9 and 0·8 per cent. of the total phosphoric acid and potash respectively.

N. H. M.

Analytical Chemistry.

The Oxy-coal-gas Flame for Spectrum Analysis. By O. VOGEL (*Zeit. anorg. Chem.*, **5**, 42—62).—The author finds that the characteristic spectra of the elements are more easily obtained in the flame of a burner fed with coal gas and compressed oxygen than in the flame of a bunsen burner. For, whilst minerals must be decomposed and their constituent metals converted into volatile salts in order that the spectra may be produced by a bunsen flame, there is no need for this preliminary treatment when an oxygen-fed flame is employed. The elements may be classified according to the ease with which they yield characteristic spectra; (I) in a bunsen flame; (II) in an oxygen-fed coal gas blow-pipe; (III) in a spark apparatus; and (IV) in an absorption spectrum apparatus.

I. Sodium, potassium (lithium), strontium, calcium, barium.

II. Barium, boron, lithium, indium, thallium, rubidium, cæsium, manganese, lead, copper, bismuth (antimony, tin, magnesium).

III. Zinc, cadmium, mercury, silver (magnesium).

IV. Magnesium, aluminium, iron, cobalt, nickel, chromium, uranium, manganese (as permanganic acid).

The most marked advantage gained by the use of the oxygen-fed

flame is in the more refrangible end of the spectrum, where the lines appear much more brightly than with the bunsen flame.

The author finds that lithium is far more widely distributed in nature than is generally supposed. A. G. B.

Quantitative Separation of Iodine, Bromine, and Chlorine: Estimation of Bromine in Mineral Waters and Mother Liquors. By P. JANNASCH and K. ASCHOFF (*Zeit. anorg. Chem.*, **5**, 8—12).—The authors depict a convenient apparatus for the separation of bromine from chlorine by the method which they have already described (this vol., ii, 295), and quote some analyses of mineral waters and mother liquors in illustration of the applicability of the method. Hydrocyanic acid may be estimated with accuracy by acidifying the solution under examination with a few drops of sulphuric acid, distilling in a current of steam, and absorbing the acid vapour in a solution of sodium hydroxide, from which the cyanide may be precipitated as silver cyanide. A. G. B.

Reduction of Nitric acid by Ferrous Salts. By C. F. ROBERTS (*Amer. J. Sci.*, **46**, 126—136).—The author has made numerous experiments to ascertain why the estimation of nitrates by means of ferrous salts generally gives results which are too low. The apparatus used consists of a small, tubulated retort, upon the neck of which is fitted a small condenser to prevent loss of liquid during the distillation. Into the tubulure of this retort is fixed tightly, by a carefully ground joint, a tube drawn out so as to dip below the surface of the liquid, and fitted with carefully ground stop-cocks, and so branched above as to make it possible to transmit carbonic anhydride through the apparatus, or to admit any liquid without air entering. The condenser is joined to a Will and Varrentrap nitrogen bulb, used as a trap, and this connected by thick vacuum tubing with a Hempel gas burette filled with aqueous soda. About 0·1 gram of the nitrate is introduced into the retort, preferably in the dry state. Carbonic anhydride, generated from marble and hydrochloric acid containing a little cuprous chloride, is passed until it is practically all absorbed by aqueous soda, and 40 c.c. of a solution of ferrous chloride is then admitted through the funnel tube after shutting off the gas and lowering the levelling tube of the burette. The liquid is then boiled until all the nitric oxide has been expelled, and its complete removal is secured by a further passage of carbonic anhydride. The volume of the gas in the burette is then noted with the usual precautions. To see how much of it consists of nitric oxide, the author prefers to absorb it by means of potassium permanganate. In some experiments, a solution of potassium iodide was introduced into the nitrogen bulbs, to reduce any higher oxides of nitrogen. As the result of many experiments, the author finally draws the following conclusions:—1. The best results are obtained when the gas is passed through solution of potassium iodide. 2. If small amounts of air have got into the apparatus, they will not affect the total volume of gas if potassium iodide be not used; but if this is used, the error will be still greatly reduced by the solubility of nitric oxide in aqueous soda. 3. On

account of this slight solubility, the gas should not be left too long in contact with the alkali. 4. If the hydrochloric acid used is very dilute, the reaction proceeds very slowly, but the result is not affected. 5. If the nitrate and the ferrous chloride are mixed whilst hot, higher oxides of nitrogen are formed, but they are again reduced by the potassium iodide. 6. If potassium iodide is used, there is no need for a large excess of iron. L. DE K.

Estimation of Chlorates and Nitrates, and of Nitrites and Nitrates in one Operation. By C. F. ROBERTS (*Amer. J. Sci.*, **46**, 231—235).—The apparatus used is the same as that required for the gas-volumetric estimation of nitric acid by means of an iron salt (see preceding abstract). The mixture, of, say, potassium chlorate and nitrate, is boiled with hydrochloric acid containing manganous chloride. Chlorine is liberated from the chlorate, but also to a certain extent from the nitrate; but the amount of the latter may be accurately determined from the volume of nitric oxide given off. By passing the chlorine through a solution of potassium iodide, estimating the liberated iodine with thiosulphate, and, allowing for the amount of chlorine generated by the nitrate, the analysis may be very accurately carried out. Of course everything depends on the correct measurement of the nitric oxide.

By the action of manganous chloride on a hydrochloric acid solution of a nitrate or nitrite, both chlorine and nitric oxide are given off and may be readily estimated. If the total weight of nitrate and nitrite is known, the proportion of each may be found by indirect analysis. The author thinks this process well suited, at all events, for the assay of commercial nitrites. L. DE K.

Rapid Estimation of Phosphorus in Iron and Steel. By W. MACFARLANE and A. WILSON (*Chem. Centr.*, 1893, ii, 145—146; from *Iron and Coal Trade Rev.*, 1893, 330).—The authors propose a standard process and also a rapid method:—1. *Standard Process.*—2 grams of the sample is dissolved in a 110 mm. wide beaker, in 15 c.c. of hydrochloric acid (sp. gr. 1·16) and 15 c.c. of nitric acid (sp. gr. 1·42). The solution is evaporated to dryness, and the beaker is put for 10 minutes on a hot plate. After cooling, the residue is dissolved in 20 c.c. of hydrochloric acid, the solution is boiled down to half, diluted with 20 c.c. of hot water, and filtered into a 700-c.c. beaker. After neutralising with ammonia, the iron is reduced by means of ammonium hydrogen sulphite, the excess of sulphurous acid is boiled off, and a slight excess of ferric chloride is added. The phosphoric acid is now precipitated as ferric phosphate by the cautious addition of ammonium carbonate; the precipitate is washed twice with hot water on a filter, and redissolved in dilute hydrochloric acid. The solution is supersaturated with ammonia, the precipitate redissolved in nitric acid, and the liquid, after heating to 85°, mixed with 200 c.c. of molybdate mixture. The precipitate is washed with dilute nitric acid (1—20), and dissolved in dilute ammonia (1—8). The solution is nearly neutralised with ammonia, magnesium mixture is added, and

then again one-sixth of the bulk of ammonia; the precipitate formed is treated as usual.

2. *The Rapid Method.*—The sample is dissolved as before and made up at once to 250 c.c.; 20·28 c.c. is put into an Erlenmeyer flask and mixed first with 2 c.c. of ammonia and then with a slight excess of hydrochloric acid; 17 c.c. of ammonium nitrate solution is added, the liquid is heated to 85°, and, after the addition of 20 c.c. of molybdate solution, it is well shaken for one minute. The precipitate is filtered off, washed three times with dilute nitric acid (1—50), rinsed into a tared dish, dried, and weighed. The weight multiplied by 10 represents the amount of phosphorus in the sample. This process is particularly suitable for the analysis of pig iron. When dealing with cast-iron, 2 grams is dissolved in 20 c.c. of nitric acid and 7 c.c. of water, the solution is evaporated to dryness and heated for five minutes on a hot plate. The residue is then treated with 15 c.c. of hydrochloric acid, evaporated to a syrupy consistence, rinsed into an Erlenmeyer flask, mixed with 15 c.c. of ammonium nitrate solution, and heated to 85°; finally, the phosphoric acid is precipitated by adding 15 c.c. of molybdate solution.

To estimate phosphoric anhydride in slags, 0·5 gram of the sample is dissolved in 8 c.c. of hydrochloric acid. After adding 12 c.c. of water, the liquid is evaporated down to 10 c.c., filtered into a 250-c.c. flask, and made up to the mark. 25 c.c. of the solution is then treated with 18 c.c. of ammonium nitrate solution, and 20 c.c. of molybdate solution, as before. L. DE K.

Volumetric Estimation of Phosphates. By C. WAVELET (*Chem. Centr.*, 1893, ii, 145; from *Schweiz. Woch. Pharm.*, **21**, 173—174).—The author recommends the volumetric lead process originally suggested by Mohr and Schwarz. The following solutions are required, 1. A standard solution containing 10·085 grams of (dry) sodium hydrogen phosphate per litre. 2. A solution of 50 grams of sodium acetate per litre. 3. A solution of 40 grams of lead nitrate per litre. 4. A 5 per cent. solution of potassium iodide, contained in a bottle made of yellow glass. 70 c.c. of the phosphate solution is mixed with 5 c.c. of the sodium acetate, and the lead is then added from the burette until precipitation ceases, the potassium iodide serving as indicator. A blank experiment, without phosphate, should also be made, and the result corrected thereby.

For the assay of commercial phosphates, 5 grams of the sample is dissolved in nitric acid and diluted to 250 c.c. 50 c.c. is then titrated with lead solution. L. DE K.

Volumetric Estimation of Pyrophosphoric acid and Alkali Pyrophosphates. By G. FAVREL (*Bull. Soc. Chim.*, [3], **9**, 446—448).—Pyrophosphoric acid acts as a monobasic acid in presence of cochineal as indicator, and as a bibasic acid in presence of soluble blue (Poirrier's C4B) at the ordinary temperature.

Alkaline pyrophosphates free from alkali hydroxides or carbonates can be directly titrated by standard acid in presence of cochineal. If alkali hydroxides be present, separate portions are titrated using

cochineal, and soluble blue respectively; the difference gives the amount of pyrophosphoric acid present. If alkali carbonates are present, the total alkali is titrated with cochineal, then, to a second portion of the liquid, the same amount of standard acid is added, and the mixture titrated with standard soda using soluble blue as indicator; the amount of soda solution used gives the amount of pyrophosphoric acid present.

In presence of phenolphthaleïn, pyrophosphoric acid requires for neutralisation 2 mols. of calcium or strontium hydroxide, or 1½ mols. of barium hydroxide. W. T.

Volumetric Estimation of Alkalis in Alkali Arsenites. By G. Favrel (*Bull. Soc. Chim.*, [3], **9**, 448—449).—Arsenious acid is indifferent to cochineal, but exerts some acid reaction on phenolphthaleïn and more on soluble blue (Poirrier's C4B).

In presence of cochineal, alkalis combined with arsenious acid can be directly titrated with standard acid. Results given show a substantial agreement between the amounts of potash determined by titration and by the platinochloride methods. W. T.

Toxicological Examination for Metals. By M. Garnier (*J. Pharm.*, [5], **28**, 193—195).—The organic matter is destroyed by oxidation with potassium chlorate, and hydrochloric acid prepared from fused purified sodium chloride and pure sulphuric acid. The metals are precipitated by sulphuretted hydrogen, slowly evolved by a continuous apparatus, and washed by passage through potash solution and distilled water in succession. W. T.

Direct Estimatien of Potassium and Sodium by means of Tartaric acid. By A. Bayer (*Chem. Zeit.*, **17**, 686—687).—The author adds to the solution a quantity of sodium carbonate sufficient to combine with any sulphuric, phosphoric, or hydrochloric acid present, and, after adding some acetic acid, tartaric acid is added in excess; the liquid is warmed for some time, mixed with one-third of its bulk of alcohol, and allowed to settle for two hours. The solution is then passed through a filter, and the precipitate of potassium hydrogen tartrate is first washed slightly with 25 per cent. alcohol and then thoroughly with 50 per cent. alcohol. It is now dissolved in boiling water, and titrated with decinormal soda, using phenolphthaleïn as indicator. The test analyses prove the method to be quite as trustworthy as the platinic chloride process.

Sodium may be estimated directly, in presence of potassium, by boiling with ammonium hydrogen tartrate and a little acetic acid. When cold, the liquid is mixed with one-third of its bulk of absolute alcohol, and, after some time, made up with 25 per cent. alcohol to a definite bulk: for instance, 250 c.c. An aliquot part, say 200 c.c., is now filtered and evaporated, with the addition of a little nitric acid, and the residue is gently ignited and then extracted with water. The sodium, after the usual treatment with barium chloride to decompose sulphates, &c., is finally weighed as chloride. As, however, potassium hydrogen tartrate is not quite insoluble in 25 per cent. alcohol, the amount of sodium chloride found will be somewhat

too high, but this may be remedied by allowing 0·0348 gram of potassium chloride for every 200 c.c. of alcoholic filtrate.

L. DE K.

Volumetric Estimation of Lead. By ALEXANDER (*Chem. Centr.*, 1893, ii, 293—294; from *Engin. and Min. Journ.*, **55**).—Ammonium molybdate causes, in a lead solution, a precipitate of lead molybdate insoluble in acetic acid. 0·5—1 gram of the sample of lead is dissolved in a mixture of sulphuric and nitric acids, and evaporated until sulphuric fumes begin to escape. When cold, the liquid is diluted with cold water, then heated for some time, and filtered; the precipitate is washed with dilute sulphuric acid, dissolved in ammonium acetate, acidified with acetic acid, and diluted with boiling water to 250 c.c. The molybdate solution is then added from a burette until all the lead is precipitated, which may be ascertained by adding a drop of the supernatant liquid to a drop of tannic acid solution (1—300), which will give a yellow colour should the least excess of molybdenum be present. The molybdate solution is prepared by dissolving 9 grams of ammonium molybdate in a litre of water to which a few drops of ammonia have been added. The analysis takes about an hour.

L. DE K.

Detection and Estimation of Lead in Tartaric and Citric acids. By R. WARINGTON (*J. Soc. Chem. Ind.*, **12**, 97—104, 222—225).—The author first calls attention to the occasional presence of visible fragments of metallic lead, probably fine scrapings of metallic lead left by plumbers when mending the leaden vessels. Both tartaric and citric acid crystals have occasionally attached to their base, where they have been in contact with the leaden vessel, patches of an opaque, whitish substance, which is evidently a portion of the corroded surface of the lead removed by the crystal. This substance does not always entirely dissolve in water, but it does so very rapidly when excess of ammonia is added. The author has, however, generally found the lead to pass into the aqueous solution. After describing the various pharmacopœia tests, British and foreign, for the detection of lead in tartaric and citric acids, the author finally recommends the following process. 40 grams of the sample is dissolved in a little water, and pure, strong ammonia is added in slight excess; the liquid is then cooled and diluted to 120 c.c. As a preliminary experiment, 10 c.c. is taken, diluted to 50 c.c., and mixed in a Nessler tube with 1 drop of solution of ammonium sulphide; the colour developed indicates what volume of solution should be taken for the determination, and this may range from 5 to 50 c.c. The tint has now to be matched with the pure solutions. A volume of *pure* ammoniacal tartrate or citrate solution identical with that taken of the acid under examination is mixed with a measured quantity of a slightly acid lead nitrate solution, containing 0·1 gram of metallic lead per litre. A drop of ammonium sulphide is then added, and, should the coloration be too light or too dark, the experiment must be repeated until a perfect match is obtained, just as in Nesslerising water. The amount of iron present in commercial tartaric or citric acid is, as a rule, too s m

with the test. A considerable amount of iron will be at once indicated by an abnormal blackish colour. The presence of copper will betray itself by a bluish coloration on adding the ammonia. Both iron and copper may, however, be rendered harmless by the addition of a drop of a solution of potassium cyanide before adding the ammonium sulphide.

As it is well-nigh impossible for a manufacturer to produce an acid absolutely free from lead, the author proposes the following standard of purity. The proportion of lead in either tartaric or citric acid should not exceed 5 parts per million, when tested by the method described.

L. DE K.

Detection of Lead in Urine. By L. K. FRANKEL (*Chem. News*, **68**, 5).—The author states that it is possible to detect 1 part of lead, dissolved in nitric acid, in 1,000,000 parts of water, by means of the deposit of peroxide formed on a platinum electrode when the solution is electrolysed. The presence of urine prevents this deposition of peroxide from the solution of the nitrate, and, instead, a deposit of lead is obtained on the negative electrode; but no deposit at all is obtained when urine containing lead that has passed through the animal system is electrolysed, even when the current has passed sufficiently long to oxidise the scum and mucus which at first collects on the surface. Therefore, to test for lead in urine, the author oxidises the organic matter with potassium chlorate and hydrochloric acid, and, subsequently, treats the solution with hydrogen sulphide.

D. A. L.

Separation of Iron, Aluminium, Manganese, Zinc, and Calcium. By B. KOSMANN (*Chem. Centr.*, 1893, ii, 155; from *Stahl. u. Eisen*, **13**, 431).—The author uses the process recommended by Riggs (compare Abstr., 1892, 916), but instead of adding ammonium acetate, solid ammonium carbonate is first added, and then a proper amount of acetic acid.

L. DE K.

Separation of Arsenic and Antimony. By L. GARNIER (*J. Pharm.*, [5], **28**, 97—99).—The author has critically examined a method given by Dragendorff for the separation of arsenic and antimony in toxicological researches.

The sulphides of these metals cannot be even approximately separated by the difference of their solubility in dilute ammonia, hence Dragendorff's method based on this difference cannot be employed in practice.

Ritter's method of treating the mixed mirror obtained by Marsh's method, in which finally the arsenic is precipitated as ammonium magnesium arsenate, is the best.

W. T.

Stability of Standard Solutions of Tartar Emetic. By H. GRUENER (*Amer. J. Sci.*, **46**, 206—208).—The author has found that solutions of tartar emetic, containing 16 grams of the salt per litre, form a deposit after several months, and that this sediment, chiefly a fungoid growth, contains a large proportion of antimony. But as the total quantity of deposit is but very slight, the strength of the solution is not greatly affected.

The fungoid growth may, however, be practically prevented by adding 20—30 grams of tartaric acid and also 1 c.c. of strong hydrochloric acid per litre. L. DE K.

Estimation of Nitrogen in Soils. By F. W. DAFERT (*Exper. Stat. Record*, **4**, 961; from *Rel. Inst. Agron. São Paulo, Brazil*, 1892).—The author recommends steam distillation for expelling the ammonia from the alkaline solution obtained in the Kjeldahl process. The danger of bumping is overcome, and the time required for distillation reduced to 6—10 minutes. When the soil contains much insoluble matter, the solutions should be filtered before distilling. N. H. M.

Estimation of Sugars by means of Fehling's Solution. By E. NIHOUL (*Chem. Zeit.*, **17**, 500).—The cuprous oxide is most conveniently collected on a tared filter and weighed as such. The author finds that filters after being immersed in alkaline copper solutions may be completely freed from copper by washing with water. Prolonged drying at 70—100° does not in the least increase the weight of the suboxide, but it is always contaminated with organic matter, and in accurate analyses an allowance of 0·3—0·4 per cent. should therefore be made.

Cuprous oxide may be readily converted into cupric oxide by treatment with nitric acid and ignition. With care, no loss will occur, Soxhlet's view that it volatilises to a certain extent as oxynitrate being erroneous. L. DE K.

Estimation of Isomaltose in Worts. By A. BAU (*Chem. Zeit.*, **17**, 499).—The author bases his process on the fact that isomaltose is not fermented by ordinary yeast, but suffers fermentation by *Saazer* yeast.

A quantity of wort is allowed to ferment with common yeast, and any invertible sugar left is then estimated in the ordinary way. A similar quantity of the wort is at the same time fermented with the *Saazer* yeast, and any sugar is then also estimated. The difference between the two determinations represents the amount of isomaltose. It must be remembered that 100 parts of isomaltose, on inversion, yield 105·3 parts of dextrose.

The presence of isomaltose may be proved qualitatively by the reaction with phenolhydrazol acetate. L. DE K.

Estimation of Glycogen. By E. PFLÜGER (*Pflüger's Archiv*, **53**, 491—492).—R. Külz (*Zeit. Biol.*, **22**, 192) points out that in the separation of proteïd from glycogen by Brücke's reagent one often obtains a persistently cloudy filtrate. This difficulty can be met by reprecipitating by alcohol, then dissolving the precipitate in 2 per cent. potassium hydroxide, neutralising with hydrochloric acid, and again adding Brücke's reagent. W. D. H.

Estimation of Fat in Milk. By WEISS (*Chem. Centr.*, 1893, ii, 159; from *Pharm. Zeit.*, **38**, 258).—The author's process (this vol.,

ii, 396), extraction of the fat by means of light petroleum, having been adversely criticised by Strassmann, attention is again called to the following important points.

1. The light petroleum containing the fat should be poured off after three hours when testing milk poor in cream; when the sample is very creamy, 12 hours should elapse. 2. A quarter of an hour before pouring off, the mixture should be once more thoroughly shaken. 3. The residual fat must be dried to constant weight, and as it obstinately retains petroleum, the temperature should be raised to 110°. 4. When reading off the volume of the petroleum layer, the temperature should be noted, and an aliquot part should be pipetted off at the same temperature. To prevent errors arising from expansion or contraction, the author recommends weighing instead of measuring the light petroleum. L. DE K.

Analysis of Butter. By E. LAVES (*Arch. Pharm.*, **231**, 356—366).—The author has examined the method of König and Hart (Abstr., 1891, 1301), and finds that it does not give more concordant results than the Reichert-Meissl-Wollny process, but it is more accurate than the other methods. A slight modification was introduced. Instead of boiling in the reflux apparatus for 3—3½ hours, the boiling is continued for ¾ hour only, using 60 c.c. of alcohol, and 7·0 grams of baryta; 50 c.c. of water (previously heated to 70—80°) is added, the mixture boiled for ¼ hour, diluted with 190 c.c. of hot water, and again raised to boiling. After being partially cooled, it is treated for five minutes with a stream of carbonic anhydride, filtered, again treated with carbonic anhydride, and boiled vigorously for five minutes in a reflux apparatus; it is then quickly cooled to 20°, filtered, and the barium in the filtrate determined by titration with N/10 sulphuric acid, using tropæolin OO as indicator; or, more accurately, by titrating with a solution of potassium dichromate (of strength equivalent to N/10 barium chloride) in the presence of alcohol and acetic acid, until a drop of the solution gives a blue colour to paper impregnated with tetramethylparaphenylenediamine. Or the barium may be precipitated as sulphate and estimated gravimetrically. C. F. B.

Sulphuric acid Hydrolysis of Butter-fat. By S. RIDEAL (*Analyst*, **18**, 165—168).—The idea of substituting sulphuric acid for alcoholic potash in effecting the saponification of butter-fat has been worked out by Kreis, and also by Pinette and others. The author has tried the process with very satisfactory results, the figures obtained being practically the same as those got by the Reichert-Meissl process.

10 c.c. of sulphuric acid of sp. gr. 1·836 is added to 2·5 grams of melted butter-fat. After a few minutes, 100 c.c. of water is added, and the mixture shaken, which causes the fatty acids to separate in white flakes. Solution of potassium permanganate is now added until the liquid acquires a pink colour, which is permanent for a few seconds. The mixture is then distilled with the usual precautions

until 80 c.c. has passed over, and the distillate is titrated with decinormal soda. L. DE K.

Discrimination of Butter from Margarin. By F. GANTTER (*Zeit. anal. Chem.*, **32**, 411—413).—The method described by the author for the estimation of cotton-seed oil in lard (this vol., ii, 440) serves equally well for the detection of margarin in butter. The iodine number for genuine butter varies from 13 to 16 when determined by the author's process (this vol., ii, 309); that of margarin is variable according to the kind of fat or oil employed in its manufacture, but always much higher, so that an iodine absorption exceeding 16 per cent. would indicate adulteration. Mixtures of butter with earth-nut oil, whose absorption is 49—51, were found to have iodine numbers corresponding with the proportions of the two fats. Genuine butter gives only a straw-yellow to reddish-yellow colour with strong sulphuric acid; most of the oils used in making margarin give a dark brown colour. M. J. S.

Detection of Heated Cotton-seed Oil in Lard. By W. G. CROOK (*Analyst*, **18**, 221).—The author recommends the following process which will detect 1 per cent. of heated cotton-seed oil in lard:—A small disc of white filter-paper, purified with hydrochloric acid and well washed, is just moistened with a 12 per cent. solution of silver nitrate and placed in the concave part of a watch-glass, which is then inverted over a cup-shaped porcelain capsule of about ½ oz. capacity, containing about 0·75 gram of the suspected sample. The capsule is now placed in an oil bath, which is then slowly heated until the temperature just reaches 115·5°. A more or less marked discoloration on the disc proves the presence of cotton-seed oil. L. DE K.

Rapid Saponification of Oils. By A. SMETHAM (*Analyst*, **18**, 193—196).—When mixtures of fatty and mineral oils are treated with alcoholic potash, some difficulty is experienced in completely saponifying the glycerides, as they are obstinately retained by the mineral oil which is generally but slightly soluble in the alcoholic liquid.

The author has greatly improved the process by adding to the usual mixture of oil and alcoholic potash about 20 c.c. of ether. The saponification is conducted in flasks of 6 oz. capacity, fitted with glass tubes 3 feet long, and is generally complete within 15 minutes. L. DE K.

Analysis of Oils. By W. FAHRION (*Chem. Zeit.*, **17**, 434—436).—The author some time ago attributed the gradual fall in the iodine number of oils to polymerisation setting in, and has since confirmed his views. When such polymerised oils are saponified, the acids seem temporarily to revert to their original condition, and the author therefore estimates the iodine number as follows. 0·15—0·25 of the oil is completely saponified with alcoholic soda, phenolphthaleïn is added, and the liquid exactly neutralised with N/2 hydrochloric acid. The iodine absorption is then estimated by means of Hübl's solution,

chloroform being, however, omitted. It appears that even apparently fresh oils are already to a certain extent polymerised, as the iodine absorptions by the author's method give results greatly in excess of the ordinary method. A sample of cotton oil, for instance, gave 104·8 per cent. by the old method, and 150 per cent. by the modified process. L. DE K.

New Method of Fat Analysis. By W. FAHRION (*Chem. Zeit.*, **17**, 610).—The author has modified Hazura's permanganate process, and operates as follows. 10 grams of the fat is saponified with 10 grams of sodium hydroxide dissolved in dilute alcohol. After the alcohol has been expelled, the soap is dissolved in 1 litre of water, and heated to boiling. According to the iodine number of the fat, 10—25 grams of potassium permanganate, dissolved in 200—500 c.c. of water, is slowly added, and the boiling is continued for some time. After filtering, the solution is acidified with hydrochloric acid, and, when quite cold, the fatty mass is collected on a cloth, well pressed, and then treated with light petroleum. The solid, also the unoxidised, portions of the fat pass into solution, whilst the oxidation products are left behind, and may be examined afterwards. In special cases, the process may be still further simplified. To test, for instance, for linoleïc acid in a non-drying oil, 10 grams of the sample is, as before, oxidised with 10 grams of permanganate. The fatty matter separated by hydrochloric acid is not, however, extracted with light petroleum, but boiled with about 1 litre of water. The liquid is filtered whilst boiling hot, the filtrate is rendered alkaline, concentrated to 100—150 c.c., and, while still warm, introduced into a separating funnel. After adding a slight excess of hydrochloric acid and cooling, the liquid is agitated with ether. If the fat contains oleïc acid only, a clear solution is obtained; but should linoleïc acid be present, a white, flocculent precipitate of tetrahydroxystearic acid will be noticed. The author has proved the presence of linoleïc acid in lard by this process. L. DE K.

Detection and Estimation of Neutral Fats in Mineral Oil. By J. KLIMONT (*Chem. Zeit.*, **17**, 543).—The author recommends the following process for the detection and estimation of small quantities of neutral fats in mineral oils. 15 grams of the sample is saponified with 100 c.c. of a 10 per cent. alcoholic solution of potassium hydroxide in a 400 c.c. flask attached to a reflux condenser. After heating for one or two hours, the contents are cooled, mixed with an equal bulk of water, and filtered through a wet filter. The filtrate is then exactly neutralised with hydrochloric acid, and agitated in a separating funnel with light petroleum. The watery layer will, if fat be present, contain potash soap, and consequently give a flocculent precipitate on the addition of calcium chloride.

The same process is suitable for a quantitative estimation of the fat. The aqueous layer is concentrated to about 100 c.c., and precipitated with calcium chloride solution. The precipitate is collected on a weighed filter, well washed, dried at 110°, and weighed. The whole is then burnt to constant weight, and the residual calcium

oxide deducted from the total weight. The fatty anhydride is then calculated to neutral fat. When the amount of fat exceeds 5 per cent., the process is no longer trustworthy. L. DE K.

Analysis of Aniline Oil. By H. REINHARDT (*Chem. Zeit.*, **17**, 413—414).—The author's process is based on the facts (1) that aniline, when treated with nascent bromine, yields a tribromo-derivative, whilst ortho- and para-toluidine give dibromo-compounds; (2) that when oxalic acid is added to a hydrochloric acid solution of the three amines, the paratoluidine is precipitated first, the aniline afterwards, and the orthotoluidine not at all. To estimate aniline, or the joint toluidines, or a mixture of the two, the author uses a solution prepared by dissolving 480 grams of bromine and 336 of pure potassium hydroxide in a litre of water, which solution must be well boiled to destroy any hypobromite, and finally diluted to 9 litres. The solution is best standardised by means of pure aniline and toluidine. To carry out an analysis of a commercial sample, about 1·5—2 grams is dissolved in 100 c.c. of hydrobromic acid (sp. gr. 1·45) and 1000 c.c. of water, and the bromine solution is then run in from a burette until a drop of the liquid gives a bluish spot on potassium iodide-starch paper. The proportion of aniline and joint toluidines is now indirectly calculated from the amount of bromine absorbed.

Or 100 grams of the sample is mixed with 106 grams of hydrochloric acid, and then with a calculated slight excess of oxalic acid dissolved in 10 times its weight of water. After 48 hours, the precipitated oxalate is collected, and slightly washed. It is then decomposed by means of aqueous potash, and the liberated oil (paratoluidine and some aniline) is collected and weighed. Any aniline is then estimated by the bromine process. The test analyses are very satisfactory. L. DE K.

Assay of Alkylanilines. By W. VAUBEL (*Chem. Zeit.*, **17**, 465—466).—The author recommends the following process. 25 grams of the sample is mixed with 50 c.c. of xylene, and when the temperature has become constant, 25 c.c. of acetic anhydride is added, and the rise in temperature is noticed. A check experiment is now made with 25 c.c. of a mixture of diethylaniline and aniline, containing as much of the latter as the sample shows when analysed by Reverdin and De la Harpe's process. The difference in the two rises in temperature is put down to the presence of monethylaniline, and its proportion is then found by referring to the author's tables. L. DE K.

Estimation of Hydrazine in Hydrazine Salts. By J. PETERSEN (*Zeit. anorg. Chem.*, **5**, 1—7)—The oxidation of hydrazine by Fehling's solution results in the elimination of the total nitrogen in the free state. This fact may be applied to the estimation of hydrazine as follows. An excess of Fehling's solution is diluted to about 60 c.c. and boiled in a flask, provided with a two-holed cork which carries a delivery tube and a glass rod, until all the air has been expelled. The weighed portion of the hydrazine salt is con-

tained in a small tube, which is closed at one end and has its open end thrust into the bottom of that hole in the cork which carries the glass rod; when the air has been expelled from the flask the glass rod is pushed down, and the small tube is thus thrust into the flask. The nitrogen is rapidly evolved and is collected in a measuring tube, boiling being continued until the expulsion of the gas is complete. A correction of $\frac{1}{10}$ c.c. is made for the air retained in the weighing tube.

When hydrazine is oxidised by potassium permanganate in the presence of a 6—12 per cent. solution of sulphuric acid, the reaction which occurs may be represented by the equation $17N_2H_4 + 13O = 13H_2O + 14NH_3 + 10N_2$. For direct titration, the solution containing the hydrazine must be at a temperature of 60—70°, and the end of the reaction must be taken as that point at which the pink colour, which is some time in completely fading, becomes darker on the addition of more permanganate. For estimation of the nitrogen evolved, the apparatus described above will serve; the hydrogen salt, together with the sulphuric acid, is placed in the flask, and the solid permanganate in the small tube. A trace of oxygen is evolved by the rapid ebullition of the permanganate with the sulphuric acid, so that the gases are collected in a Bunte's burette and this oxygen absorbed before reading the volume of the nitrogen. The estimation of the ammonia is effected by distillation with alkali in the usual manner. A. G. B.

Detection of Alkaloïds, "Saccharin," and Salicylic acid. By Lindeman and Motteu (*Bull. Soc. Chim.*, [3], **9**, 441—446).—The authors have applied the principle of partition of a dissolved substance between two non-miscible solvents to the examination of organic substances and liquids for alkaloïds, "saccharin," and salicylic acid.

A solvent having, in comparison with water, a high coefficient of partition is employed. The liquids are carefully placed in contact without mixing; if the aqueous solution be turbid, it is separated from the other solvent by a parchment partition to avoid the introduction of solid particles into the new medium. If the liquid layers are arranged so as not to be thicker than 1 cm., the partition is complete in 24 hours, and the new solvent can be evaporated off and its residue examined.

The examination of beer, milk, coffee, foods, and the body of a poisoned dog has been carried out, known small quantities of strychnine being introduced, and chloroform employed for extraction. Similarly morphine has been determined in beer and urine by chloroform and by amyl alcohol, quinine in beer by chloroform, "saccharin" (benzoicsulphinide) in beer by ether, and salicylic acid in wine and beer by benzene. W. T.

Volumetric Estimation of the Alkaloïds and of some Metals. By D. Vitali (*L'Orosi*, **16**, 181—186).—The metals copper, mercury, cadmium, silver, gold, platinum, antimony, and tin, which are completely precipitated from neutral solutions by hydrogen sulphide,

and whose sulphides are insoluble in dilute acids, may be determined in the following manner. The metallic salt (0·5—1·0 gram) is dissolved in distilled water (25—30 c.c.), the solution freed from air by prolonged boiling and precipitated with hydrogen sulphide, care being taken to avoid any contact with the air. The solution is then filtered, the precipitate washed with boiled water, and the filtrate made up to a known volume. On titrating the solution with standard alkali, the amount of acid originally combined with the metal is found, and hence the percentage of the metal itself may be deduced.

Solutions of the hydrochlorides or sulphates of the alkaloïds may be precipitated with silver or lead nitrate respectively, and the metal estimated in the precipitate by conversion into sulphide as described above. A simple calculation then gives the proportion of acid in the alkaloïdal salt, and consequently the quantity of the alkaloïd itself. Both the above methods give good results. W. J. P.

Titration of Morphine. By CANNEPIN and VAN EIJK (*Bull. Soc. Chim.*, [3], **9**, 437—441).—The chief sources of error in Portes and Langlois' method have been obviated by following the process detailed below. The original method gave the highest and most concordant results of any of the ordinary processes. The most important sources of loss are—(1) morphine remaining in solution on precipitation, (2) morphine dissolved in the wash water, (3) morphine not extracted from the opium sample by the process.

By the use of lime (3) is rendered very small, and (2) and (1) are largely avoided by using the solutions of morphine indicated below.

10 grams of opium and 4 grams of slaked lime are gradually intimately mixed with 100 c.c. of a solution of 0·805 gram morphine hydrochloride per litre, digested for half an hour, and filtered. 20 c.c. of the filtrate is evaporated at 100°, and the residue weighed. 50 grams (*plus* the weight of solid residue from half the opium, in all about 52 grams) of the filtrate is weighed out, and shaken up with 10 c.c. of ether until saturated; 0·5 gram of ammonium chloride is added, the whole allowed to remain two hours, and then filtered; the precipitated morphine is thoroughly washed with a saturated solution of morphine (0·42 gram crystallised morphine per litre) and dried at 98°. The precipitate may be examined polarimetrically in dilute acetic acid solution, or titrated, using cochineal as indicator. W. T.

Coniine and Nicotine. By G. HEUT (*Arch. Pharm.*, **231**, 376—378).—These may be distinguished by adding phenolphthaleïn and chloroform to their aqueous solution and shaking vigorously; in the case of nicotine, the colour then disappears at once; with coniine, it is permanent.

To estimate coniine and nicotine in the presence of each other, dissolve in a small quantity of water, with addition of alcohol; to 50 c.c. of the solution, add 5 drops of chloroform and 1 drop of strong solution of phenolphthaleïn, and titrate with N/10 sulphuric acid until,

on shaking vigorously, the colour disappears; this gives the coniine. To determine the nicotine, now add litmus, and continue the titration with acid. (The colour reaction with litmus is not affected by chloroform.) C. F. B.

Rapid Estimation of Caffeïne in Tea and Coffee. By GUILLOT (*Chem. Centr.*, 1893, i, 865; from *Apoth. Zeit.*, **8**, 132).—5 grams of finely-powdered tea is boiled for 20 minutes with 100 c.c. of water, water being added occasionally during the boiling, to restore the loss caused by evaporation. 5 grams of lime is then added, and, after the boiling has been continued for another 15 minutes, the mixture is filtered through a small wet cloth, and the insoluble matter again boiled with 50 c.c. of water, this operation being once more repeated. The united filtrates are now put into a 500 c.c. stoppered separatory funnel, and agitated three times in succession with 60 c.c. of chloroform. When clear, the chloroform is drawn off, filtered through cotton-wool, and evaporated in a tared dish.

The residual caffeïne is fairly pure. When applying the process to coffee, this must be coarsely ground, dried, and reduced to a fine powder. It is then boiled with water first for half an hour, then again twice for a quarter of an hour, and finally treated like the tea decoction. L. DE K.

Separation of Theobromine and Caffeïne. By H. BRUNNER and H. LEINS (*Chem. Centr.*, 1892, i, 802; from *Schweiz. Woch. Pharm.*, **31**, 85—87).—Süss extracts the raw material with light petroleum to remove caffeïne and fatty matter, and then with chloroform to dissolve the theobromine. The authors found, however, that the alkaloïd obtained in this way is not pure, but reduces an ammoniacal solution of silver nitrate, whilst the pure substance yields a white compound of the formula $C_7H_7AgN_4O_2$.

When pure, theobromine may be separated from caffeïne by means of silver nitrate. About 0·2 or 0·5 gram of the mixed alkaloïds is dissolved in 200 c.c. of water, mixed with 5 c.c. of ammonia, and boiled with 0·6 gram of silver nitrate until the ammonia is expelled. The liquid is cooled to 30°, the precipitate collected and washed with water at 30°, and then dried at 110°. L. DE K.

Estimation of Alkaloïds. By A. GRANDVAL and H. LAJOUX (*J. Pharm.* [5], **28**, 99—103 and 152—156).—*Estimation of Emetine in Ipecacuanha Root.*—The powdered root is extracted with a mixture of alcohol and ether (3 : 8 parts), rendered ammoniacal by the addition of ammonia solution (2 parts), and washed with ether. The ethereal solution is agitated with a little dilute sulphuric acid, separated, and washed until free from alkaloïd. The acid solutions are mixed, rendered alkaline with soda, and again extracted with ether. The ethereal extract, on evaporation, yields the alkaloïd in a nearly pure state.

Such alkaloïds as emetine and sparteïne are not, as sometimes supposed, destroyed by the dilute acid and alkaline solutions used. Better results are obtained with caustic soda than with carbonates or bicarbonates.

Estimation of Cocaïne and Separation of Cocaïne and Ecgonine.—The alkaloïds from powdered coca leaves are extracted as above, the acid solution being washed free from colouring matters with ether before adding soda. The alkaloïds are then neutralised by hydrobromic acid, and powdered potassium bromide added to saturation. The double bromide of cocaine and potassium separates out, and is washed free from ecgonine by means of a cold saturated solution of potassium bromide. The cocaïne is then obtained in the crystalline condition by treatment with soda and extraction with ether.

This method becomes general in its application to alkaloïds insoluble in ether, provided a suitable solvent is used.

Estimation of Alkaloïds with Previous Separation by Potassium Mercury Iodide.—The substance is treated with lead acetate, and extracted with water until the washings give no precipitate with potassium mercury iodide; most of the organic acids present remain as insoluble lead compounds, together with much of the colouring and extractive matter and a large proportion of the proteïds. Dilute sulphuric acid is added to the solution obtained, and the lead sulphate filtered off; the alkaloïds are then precipitated from the filtrate by means of potassium mercury iodide; variable amounts of albumin and colouring and extractive matters also coming down. After standing some time, the precipitate is collected and treated by one of the following processes:—(1) Potassium cyanide solution, a little soda, and ether or other appropriate solvent are well shaken with the precipitate. The ethereal solution is caused to separate from the emulsion produced, by the addition of a little olive oil, and is then treated with sulphuric acid as above; this acid solution is washed free from adherent olive oil by agitating it with ether, and is then treated as above with soda and ether, so as to recover the alkaloïds in the free state. In this process the mercury is dissolved by potassium cyanide, hydriodic acid is eliminated by soda, and the freed alkaloïd is dissolved by the immiscible solvent. (2) The decomposition of the precipitate is accomplished by digestion with a slight excess of sodium sulphide, and the extraction of the freed alkaloïd is carried out as in the first method. The latter process is considered preferable by the authors.

Liquid alkaloïds, in general, cannot be separated by this method, but sparteïne forms an exception to the rule.

Atropine is not entirely precipitated by potassium mercury iodide; hence the process cannot be advantageously employed for the extraction of alkaloïds from belladonna. W. T.

Estimation of Resin in Soaps. By J. Lewkowitsch (*J. Soc. Chem. Ind.*, **12**, 503—508).—The author (Abstr., 1891, 509) has thoroughly investigated Gladding's original silver process for the estimation of resin in fatty acid mixtures; also modifications of the same proposed by Hübl and Stadler and by Grittner and Szilazi. The results, as shown by the tables, prove the method to be utterly untrustworthy. The process recommended by Twitchell (conversion of the fatty acids into ethyl compounds), which may be carried out either gravimetrically or volumetrically, also failed, in the author's hands, to give anything

like an approximate result. This method is, however, comparatively new, and requires further independent investigation (compare Abstr., 1892, 389). L. DE K.

Qualitative Analysis of Coal-tar Colouring Matters. By A. G. GREEN (*J. Soc. Chem. Ind.*, **12**, 3—7).—The author employs a solution of tannin for distinguishing between acid and basic colouring matters, and has also adopted the division into those soluble and those insoluble in water. The chief reagents used are:—A solution containing 10 per cent. of tannin and 10 per cent. of sodium acetate; zinc dust, in conjunction with hydrochloric acid or ammonia; a solution containing 1 per cent. of chromic acid (for basic colours); a solution containing 1 per cent. of chromic acid, or potassium dichromate and 5 per cent. of sulphuric acid (for acid colours).

When the sample is soluble in water, its behaviour towards tannin is first ascertained, and the liquid is next reduced by zinc dust and hydrochloric acid. A drop of the now colourless liquid is put on to filter paper, and mixed with a drop of the chromic acid solution. This will cause different colorations, according to the nature of the dye, as indicated by reference to the author's tables.

Insoluble colours are treated with weak aqueous soda, and reduced by zinc dust and ammonia. If the soda refuses to dissolve the colour, alcohol must be used. The solution is then further examined, as directed in the special table. L. DE K.

Albumin and Sugar in Urine. By BENNO-LAQUER (*J. Pharm.* [5], **28**, 134—135).—The clear, filtered urine is heated to boiling, and a tenth of its volume of nitric acid added in one operation. If a flocculent and persistent precipitate forms, the urine is albuminous. To the clear solution, cooled and filtered if necessary, 10—20 drops of Almen's solution is added, and the test heated again for 1—2 minutes. Sugar is indicated by a dark brown coloration.

Almen's solution is prepared by dissolving 4 grams of Rochelle salt in 100 parts of a 10 per cent. solution of soda, and digesting this liquid with 2 grams of bismuth subnitrate until mostly dissolved. This solution indicates glucose more readily than Fehling's solution, and is not affected by uric acid or creatinine. W. T.

Valuation of Hide Clippings for Glue making. By F. GANTTER (*Zeit. anal. Chem.*, **32**, 413—415).—For this purpose, it is necessary to estimate the insoluble mechanical impurities, the gelatin, and the soluble constituents which are not gelatin. The first are ascertained by boiling the substance with water until dissolved, and allowing the solution to clarify, when sand, &c., will subside, and fat will rise to the surface. The clear solution from 100 grams of the substance (boiled with 1 litre of water to which a few drops of soda solution have been added) is made up to 2 litres, and 20 c.c. of it evaporated, dried at 105°, weighed, and incinerated. This gives the total amount of ash-free organic matter. Another 10 c.c., diluted with 30 c.c. of water and neutralised with acetic acid, is treated with tannin solution until no further precipitation takes place, and then made up to

100 c.c. The excess of tannin is removed from the filtrate by hide powder, and the amount of organic matter in 50 c.c. is then ascertained as above. The gelatin can be calculated from the difference.

M. J. S.

Discrimination between Genuine and Exhausted Ginger. By B. DYER and J. F. H. GILBARD (*Analyst*, **18**, 197—200).—The authors recommend taking the alcoholic extract, after first extracting the sample with ether. In genuine gingers, it ranges from 2·1 to 3·8 per cent.; in the exhausted samples, from 0·8 to 1·4 per cent. They also attach great value to the constitution of the ash, which, in genuine samples (excluding sand) ranges from 3·1 to 4·1 per cent., whilst, in exhausted samples, it is only 1·1 to 2·3 per cent. The ash soluble in water is especially important, as, in genuine samples, it ranges from 1·9 to 3 per cent., whilst, in exhausted samples, it is 0·2 to 0·5 per cent.

The authors, whilst not denying that some samples of ginger may be mixed with a considerable amount of exhausted ginger without fear of detection, still hope that their process will be useful to prove a flagrant adulteration of the drug. L. DE K.

Estimation of Fibre in Foods by means of the Centrifugal Apparatus. By W. THÖRNER (*Chem. Zeit.*, **17**, 394—395).—About 1 gram of the sample is freed from fatty matter by means of ether. The operation is conducted in a special tube, which is rotated for a few minutes in the author's centrifugal machine. The ether can then be poured off without any loss of insoluble matter. After the layer of ether has been removed, the tube is filled with dilute sulphuric acid, and placed in boiling water for 30 minutes to cause the starchy matter to dissolve. The insoluble matter takes a long time to settle, but when the tube is placed in the machine and rotated for four minutes at a speed of 2000 revolutions per minute, the residue completely separates as a compact mass at the bottom of the tube, and the supernatant liquid may then be poured on to a weighed filter. The insoluble matter is then treated with 40 c.c. of hot water for 10 minutes, and the tube is once more whirled. After pouring off the washings, the fibre is heated with dilute aqueous potash to remove nitrogenous matters and again whirled.

The fibre is finally transferred to the filter, well washed with water, alcohol, and ether, and dried to constant weight. It should, of course, be tested for mineral matter. The process gives very concordant results, and with a moderate-sized machine, eight estimations may be completed within three or four hours. L. DE K.

Estimation of Silk in Fabrics. By F. W. RICHARDSON (*J. Soc. Chem. Ind.*, **12**, 426—431).—The author recommends the following process:—25 grams of crystallised nickel sulphate is dissolved in 500 c.c. of water; the nickel is then completely precipitated as hydroxide by sodium hydroxide, and thoroughly washed. The precipitate is rinsed into a 250-c.c. flask with 125 c.c. of water; the flask is then filled to the mark with ammonia of 0·88 sp. gr., and well

shaken. Silk is rapidly dissolved in this solution, even in the cold, whilst cotton and wool are practically insoluble.

To dissolve silk from plush, a 10 minutes' boiling under a reflux condenser is required. In the cold, cotton loses 0·4 per cent.; on boiling, 0·8 per cent. of its weight. L. DE K.

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ERRATA.

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Page	Line	
141	19,	*for* "there is first formed" *read* "we may suppose that there is first formed."
784	18*	„ "in 1882" *read* "in 1882, but these compounds are quite distinct from Recoura's chromosulphuric acid."
1183	11	„ "a crystalline bromo-additive product when treated with bromine water" *read* "a crystalline additive product with hydrogen bromide."
1228	15	„ "143°" *read* "145°."
1509	8	„ "proteïds" *read* "albumen."

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PART I.

17	3*	„ "L. VOLPYAN" *read* "L. VOLPJAN."
21	2*	„ "A. NEMIROFFSKY" *read* "A. NEMIROVSKY."
23	13*	*et seq.*, in the names in italics, *for* "*-idine*" *read* "*-idene.*"
39	15,	*for* "**1 : 4-Amidonaphthalene**" *read* "**1 : 4-Ethoxyamidonaphthalene.**"
52	6*	„ "*di-β-naphthyl-αγ-diketo-βδ-diethylpiperazine*" *read* "*di-β-naphthyl-αγ-diketo-βδ-dimethylpiperazine.*"
53	15	„ "*a-ethoxyisobutyro-β-naphthalide*" *read* "*a-ethoxyisobutyro-a-naphthalide.*"
105	12	„ "and equal" *read* "although not equal."
127	2	„ "SCHIFFER" *read* "SCHIFFERER."
168	2*	„ "K. BRUNCK" *read* "R. BRUNCK."
179	16*	„ "180°" *read* "280°."
180	6	„ "R. v. ROTTENBURG" *read* "R. v. ROTHENBURG."
304	17	„ "R. ANSCHÜTZ" *read* "R. AÑSCHÜTZ and W. MONTFORT."
307	15	„ "R. BRAUNSCHWEIG" *read* "J. W. BRÜHL and R. BRAUNSCHWEIG."
357	5*	„ "Beckmann" *read* "Elbs (Abstr., 1892, 347)."
379	4	„ "A. SOLDIANI" *read* "A. SOLDAINI."
387	1	„ "**Witt's Oxycellulose.** By A. NASTNIKOFF" *read* "**Witz's Oxycellulose.**" By A. NASTIUKOFF."
420	22, 23	„ "S. JUKOFFSKY" *read* "S. JUKOVSKY."
451	18	*et seq.*, *for* "ferment" *read* "enzyme."
451	22*,	*for* "fermenting" *read* "hydrolytic."
451	9*	*et seq.*, *for* "to ferment" *read* "to hydrolyse."
451	4*	„ „ "fermenting" „ "hydrolysing."
506	23*	*for* "**Orthiodosobenzene**" *read* "**Orthochloriodosobenzene.**"
524	21,	*for* "**Zinc**" *read* "**Zinc Chloride.**"
580	15	„ "STAPELBERG" *read* "E. STAPELBERG."
582	23*	„ "last abstract" *read* "this vol., i, 580."

* From bottom.

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Part I (*cont.*).

Page	Line	
615	10, 11, 17,	*for* "δ-achroglobulin" *read* "δ-achroglobin."
618	3*,	*for* "V. Kistyakoffsky" *read* "V. Kistyakovsky."
632	20* „	"R. T. Mamert" *read* "R. Thomas-Mamert."
675	18 „	"W. Göhlich" *read* "E. Schmidt and W. Göhlich."
713	2* „	"V. Villiger" *read* "A. Baeyer and V. Villiger."
719	16* „	"*Ber.*, **24**" *read* "*Ber.*, **26**."
728	4* „	"$OH{\cdot}C_9NH_8Me{<}^{CO}_{C}$" *read* $OH{\cdot}C_9NH_8Me{<}^{CO}_{O}$."
729	12* „	"*Ber.*, **25**" *read Ber.*, **26**."
741	4* „	"G. Voorhees" *read* "C. G. Voorhees."

Part II.

9	12* „	"V. Kistyakoffsky" *read* "V. Kistyakovsky."
43	7 „	"**Nitrate**" *read* "**Nitrite.**"
107	1 „	"**Electrical into Chemical**" *read* "**Chemical into Electrical.**"
138	23 „	"algæ" *read* "mosses and algæ."
„	27 „	"distinct" *read* "distinct in the *Nostocs*."
„	28 „	"similar alga" *read* "alga."
444	3* „	"trimethylene" *read* "trimethylethylene."
453	23* „	"A. Gassman" *read* "A. Gassmann."
531	11* „	"**Colombous**" *read* "**Columbous.**"
532	14,*	*after* "**Thorium**" *insert* "**Oxides.**"
538	13,*	*for* "W. Lindgren" *read* "W. Lindgren and W. H. Melville."
560	1 „	"C. Keller" *read* "G. Kottmayer."
601	10* „	"phenolhydrazol" *read* "phenylhydrazine."

* From bottom.

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